

Insertion, protonolysis and photolysis reactivity of a thorium monoalkyl amidinate complex

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A. Experimental Details

General Considerations. Unless otherwise stated, all reactions were performed under an atmosphere of dry N₂ using standard Schlenk line techniques or in an MBraun N₂ atmosphere glovebox (<1.0 ppm of O₂/H₂O). All solvents were dried and degassed using a commercially available Phoenix SDS from JC Meyer Solvent Systems. All glassware, syringes, and cannulas were stored in a 140 °C oven for a minimum of 16 h prior to use. Deuterated solvents were vacuum-transferred from flasks containing sodium/benzophenone (C₆D₆, C₆D₁₂) or calcium hydride (CDCl₃), degassed with three freeze–pump–thaw cycles, and stored over molecular sieves. ThCl₄(DME)₂,¹ Li(BIMA)(THF),² ThCl(BIMA)₃,³ Th(CH₂SiMe₃)(BIMA)₃ (**1**),³ *p*-tolyl azide,⁴ and KPHMes⁵ were prepared according to previously reported literature procedures. 2,6-diisopropylaniline was purchased from SigmaAldrich and distilled prior to use. 2,6-di-*tert*-butylphenol was sublimed prior to use. Benzonitrile was dried over CaH₂ and distilled prior to use. CO gas was purchased from Praxair, Inc. and used directly from the cylinder without purification. All other reagents were purchased from commercial sources and used as received. Unless otherwise stated, NMR spectra were collected at ambient temperature on a Bruker AV-300, AVB-400, AV-500, or AV-600 spectrometer. ¹H and ¹³C{¹H} NMR chemical shifts (δ) are reported in ppm and were calibrated to residual solvent peaks. ¹¹B{¹H} and ³¹P NMR shifts (δ) are referenced to an external standard (BF₃·Et₂O and H₃PO₄, respectively). Photo-activation reactions were conducted using a Rayonet reactor (model RPR-100) centered at 253 nm or a Newport 67005 Arc Lamp Housing containing a xenon arc lamp operating at 300 W. Melting points were determined on an Optimelt SRS instrument using capillary tubes sealed under dry N₂. Elemental analysis samples were sealed under vacuum and analyzed at either the London Metropolitan University or the University of California, Berkeley. Infrared spectra were collected on a Thermo Scientific Nicolet iS10 FTIR spectrophotometer using Nujol mulls pressed between KBr plates.

Synthesis of Th(BIMA)₄ (2**):** Solid ThCl₄(DME)₂ (2.49 g, 4.49 mmol) and Li(BIMA)(THF) (4.01 g, 18.2 mmol) were added to a 250 mL Schlenk flask containing a magnetic stir bar and suspended in toluene (60 mL). The suspension was then heated to 90 °C and stirred for 5 d, upon which the solution became slightly orange and contained a colourless precipitate. The volatiles were removed under reduced pressure, and the resulting solid was triturated with hexanes (2 x 30 mL), extracted into hexanes (2 x 50 mL), filtered through Celite, and concentrated to 15 mL. The solution was stored at -40 °C overnight, yielding **2** as analytically pure, colourless crystals (2.35 g, 65.6%). ¹H NMR (600 MHz, C₆D₆): δ 3.72 (sept, CHMe₂, 8H, ³J_{H,H} = 6.6 Hz), 1.80 (s, NC(CH₃)N, 12H), 1.30 (d, CHMe₂, 48H, ³J_{H,H} = 6.6 Hz). ¹³C{¹H} (151 MHz, C₆D₆): δ 174.2 (NCN), 48.9 (CHMe₂), 25.3 (CHMe₂), 14.8 (NC(CH₃)N). Anal. Calcd for C₃₂H₆₈N₈Th (797.0): C, 48.23; H, 8.60; N, 14.06. Found: C, 48.25; H, 8.71; N, 13.93. Mp: 150 °C (decomp.). FTIR (Nujol): 2595 (w), 1495 (s), 1358 (s), 1340 (s), 1310 (s), 1187 (s), 1175 (s), 1137 (m), 1118 (s), 1044 (m), 1007 (s), 943 (w), 798 (s), 722 (w), 618 (s), 577 (m), 542 (m). Crystals suitable for single-crystal X-ray diffraction studies were grown from a concentrated hexanes solution stored at -35 °C for 16 h.

Synthesis of Th[(*p*-tolyl)NNN(CH₂SiMe₃)-κ²N^{1,2}](BIMA)₃ (3): Solid **1** (0.303 g, 0.408 mmol) was added to a 20 mL scintillation vial containing a magnetic stir bar and dissolved in 4 mL toluene. To this stirred solution was added neat *p*-tolyl azide (0.056 g, 0.421 mmol), resulting in an immediate solution colour change from colourless to gold. The solution was allowed to stir at ambient temperature for 20 min. The volatiles were removed under reduced pressure, and the resulting solid was triturated with hexane (2 x 4 mL) and extracted into HMDSO (6 mL). The solution was concentrated to 2 mL, filtered through Celite, and placed in the freezer at -35 °C for 16 h, resulting in isolation of **3** as a tan solid (0.295 g, 83.4%). ¹H NMR (600 MHz, C₆D₆): δ 7.81 (m, CH_{ptolyl}, 2H), 7.19 (m, CH_{ptolyl}, 2H), 3.99 (s, CH₂SiMe₃, 2H), 3.64 (sept, CHMe₂, 6H, ³J_{H,H} = 6.6 Hz), 2.26 (s, CH_{3,ptolyl}, 3H), 1.68 (s, NC(CH₃)N, 9H), 1.16 (d, CHMe₂, 36H, ³J_{H,H} = 6.6 Hz), 0.45 (s, CH₂SiMe₃, 9H). ¹³C {¹H} NMR (151 MHz, C₆D₆): δ 174.0 (NCN), 150.8 (C_{ptolyl}), 132.0 (C_{ptolyl}), 129.2 (C_{ptolyl}), 120.8 (C_{ptolyl}), 49.9 (CH₂SiMe₃), 48.6 (CHMe₂), 25.1 (CHMe₂), 21.2 (H₃C_{ptolyl}), 13.7 (NC(CH₃)N), 1.55 (CH₂SiMe₃). Anal. Calcd for C₃₅H₆₉N₉SiTh (876.1): C, 47.98; H, 7.94; N, 14.39. Found: C, 47.98; H, 7.88; N, 14.18; Mp: 180 °C (decomp.) FTIR (Nujol): 1489 (s), 1344 (s), 1312 (m), 1243 (w), 1199 (m), 1173 (w), 1123 (w), 1051 (w), 1013 (w), 980 (w), 852 (m), 821 (w), 805 (w), 722 (w). Crystals suitable for single-crystal X-ray diffraction studies were grown from a concentrated diethyl ether solution stored at -35 °C for 48 h.

Generation of Th[(*p*-tolyl)N(SiMe₃)](BIMA)₃ (4): Solid **3** (0.010 g, 0.0114 mmol) was added to a 4 mL dram vial and dissolved in C₆D₆ (0.6 mL). The solution was transferred to a *J*-Young NMR tube sealed with a Teflon screw cap and heated at 70 °C for 48 h, resulting in clean conversion to **4** as judged by ¹H NMR spectroscopy. ¹H NMR (600 MHz, C₆D₆): δ 7.22 (m, CH_{ptolyl}, 2H), 7.11 (m, CH_{ptolyl}, 2H), 3.60 (sept, CHMe₂, 6H, ³J_{H,H} = 6.5 Hz), 2.26 (s, CH_{3,ptolyl}, 3H), 1.74 (s, NC(CH₃)N, 9H), 1.20 (d, CHMe₂, 36H, ³J_{H,H} = 6.5 Hz), 0.55 (s, SiMe₃, 9H). ¹³C {¹H} NMR (151 MHz, C₆D₆): δ 174.4 (NCN), 151.0 (C_{ptolyl}), 130.5 (C_{ptolyl}), 123.5 (C_{ptolyl}), 48.4 (CHMe₂), 25.1 (CHMe₂), 20.8 (H₃C_{ptolyl}), 15.6 (NC(CH₃)N), 3.40 (SiMe₃). Crystals suitable for single-crystal X-ray diffraction studies were grown from a concentrated pentane solution stored at -35 °C for 7 d.

Synthesis of Th[η²-(C=N)-2,6-Me₂-C₆H₃(CH₂SiMe₃)](BIMA)₃ (5): Solid **1** (0.400 g, 0.538 mmol) and 2,6-dimethylphenyl isocyanide (0.0717 g, 0.547 mmol) were combined in a 100 mL Schlenk flask containing a magnetic stir bar and dissolved in toluene (10 mL). The solution was then heated to 65 °C and stirred for 16 h. The volatiles were removed under reduced pressure, and the resulting solid was triturated with hexane (2 x 4 mL) and extracted into HMDSO (6 mL). The solution was then filtered through Celite, concentrated to ~0.6 mL and placed in the freezer at -35 °C for 16 h, resulting in off-white crystals of **5** (0.383 g, 81.3%). ¹H NMR (600 MHz, C₆D₆): δ 7.06 (d, *m*-CH_{Xyl}, 2H, ³J_{H,H} = 7.5 Hz), 6.96 (t, *p*-CH_{Xyl}, 1H, ³J_{H,H} = 7.5 Hz), 3.85 (sept, CHMe₂, 6H, ³J_{H,H} = 6.6 Hz), 2.85 (s, CH₂SiMe₃, 2H), 2.18 (s, CH_{3,Xyl}, 6H), 1.78 (s, NC(CH₃)N, 9H), 1.28 (d, CHMe₂, 36H, ³J_{H,H} = 6.6 Hz), 0.11 (s, CH₂SiMe₃, 9H). ¹³C {¹H} NMR (151 MHz, C₆D₆): δ 289.2 (-C=NH₃C₆Me₂), 174.3 (NCN), 152.6 (C_{Xyl}), 129.2 (C_{Xyl}), 128.2 (C_{Xyl}), 124.2 (C_{Xyl}), 48.4 (CHMe₂), 35.0 (CH₂SiMe₃), 25.4 (CHMe₂), 19.2 (-C=NH₃C₆Me₂), 15.5 (NC(CH₃)N), 1.1 (CH₂SiMe₃). Anal. Calcd for C₃₇H₇₁N₇SiTh (874.2): C, 50.84; H, 8.19; N, 11.22. Found: C, 50.73; H, 8.00; N, 11.44. Mp: 198(4) °C. FTIR (Nujol): 1497 (s, ν_{C=N}), 1377

(s), 1357 (s), 1336 (s), 1316 (s), 1248 (m), 1196 (s), 1174 (s), 1124 (m), 1093 (m), 1051 (m), 1012 (m), 860 (s), 802 (m), 762 (m), 692 (w), 672 (w), 622 (w), 575 (w), 481 (w), 431 (w). Crystals suitable for single-crystal X-ray diffraction studies were grown from a concentrated pentane solution stored at -35 °C for 16 h.

Synthesis of Th[OC(=CH₂)SiMe₃](BIMA)₃ (6): Solid **1** (0.500 g, 0.673 mmol) was added to a 100 mL Schlenk tube containing a magnetic stir bar and dissolved in hexanes (30 mL). CO gas (16.5 mL, 0.673 mmol) was slowly added via syringe directly into the stirred solution over the course of two minutes at ambient temperature, during which the colourless solution became light green. The solution was then sealed off, and allowed to stir at ambient temperature for 24 h. During this time the solution became nearly colourless. The volatiles were removed under reduced pressure, and the resulting residue was extracted into pentane (10 mL), filtered through Celite, and concentrated to <0.5 mL. The super saturated solution was placed in the freezer at -35 °C for 16 h, resulting in colourless crystals of **6** (0.330 g, 63.6%). ¹H NMR (600 MHz, C₆D₆): δ 5.07 (d, H₂C=, 1H, ²J_{H,H} = 1.0 Hz), 4.79 (d, H₂C=, 1H, ²J_{H,H} = 1.0 Hz), 3.66 (sept, CHMe₂, 6H, ³J_{H,H} = 6.3 Hz), 1.71 (s, NC(CH₃)N, 9H), 1.28 (d, CHMe₂, 36H, ³J_{H,H} = 6.3 Hz), 0.39 (s, SiMe₃, 9H). ¹³C{¹H} NMR (151 MHz, C₆D₆): δ 173.0 (NCN), 104.7 (=CH₂), 48.5 (CHMe₂), 25.2 (CHMe₂), 13.0 (NC(CH₃)N), -0.6 (CH₂SiMe₃). Anal. Calcd for C₂₉H₆₂N₆OSiTh (771.0): C, 45.18; H, 8.11; N, 10.90. Found: C, 44.96; H, 8.04; N, 10.94. Mp: 130 °C (decomp.). FTIR (Nujol): 1490 (s, ν_{C=C}), 1377 (s), 1360 (s), 1331 (s), 1314 (s), 1254 (w), 1243 (m), 1219 (m), 1200 (s), 1174 (m), 1123 (m), 1051 (w), 1014 (m), 996 (s), 850 (s), 837 (s), 804 (m), 754 (w), 722 (w), 678 (w), 621 (w), 575 (w), 543 (w). X-ray quality crystals were grown from a mixture of **6** and **7**, as described below.

Generation of Th[OC(=CH₂)SiMe₃](BIMA)₃ (6) and

Th[OC(N^{*i*}Pr)C(CH₂SiMe₃)(C(Me)N(^{*i*}Pr))O-κ²O,O'](BIMA)₂ (7): Solid **1** (0.500 g, 0.673 mmol) was added to a 75 mL Schlenk tube containing a magnetic stir bar and dissolved in toluene (10 mL). CO was vigorously bubbled through this stirred solution for 5 min., during which the colourless solution became light green. The bubbling was then discontinued, and the tube sealed under an atmosphere of CO. The solution was then stirred at ambient temperature for 1 h, at which point the solution had become colourless. The volatiles were removed under reduced pressure, and the resulting residue was triturated with pentane (2 x 5 mL) and extracted into pentane (10 mL). The solution was filtered through Celite and concentrated to <0.5 mL. The super saturated solution was then placed in the freezer at -35 °C for 48 h, resulting in a microcrystalline solid (0.425 g) which contained both **6** and **7**. Despite repeated crystallization attempts, separation of **6** and **7** could not be achieved due to their similar solubility in non-polar solvents. Complex **6** could be identified by ¹H NMR spectroscopy. X-ray quality crystals were grown from a concentrated pentane solution stored at -35 °C for 72 h. Individual crystals of **6** and **7** were selected from a mixture of crystals and distinguished based upon their unit cell.

Generation of Th[-N=C(Ph)(CH₂SiMe₃)](BIMA)₃ (8): Solid **1** (0.020 g, 0.027 mmol) was added to a 4 mL dram vial and dissolved in C₆D₆ (0.3 mL). In a separate dram vial, benzonitrile (0.0083 g, 0.081 mmol) was weighed out and dissolved in C₆D₆ (0.3 mL). The two solutions were then combined and added to a *J*-Young NMR tube sealed with a Teflon screw cap. The

solution was then heated at 100 °C for 3 d, resulting in >95% conversion to **8** as judged by ¹H NMR spectroscopy. ¹H NMR (300 MHz, C₆D₆): δ 7.89 (m, CH_{Ar}, 2H), 7.17-7.27 (m, CH_{Ar}, 3H), 3.67 (sept, CHMe₂, 6H, ³J_{H,H} = 6.4 Hz), 2.73 (s, CH₂SiMe₃, 2H), 1.73 (s, NC(CH₃)N, 9H), 1.23 (d, CHMe₂, 36H, ³J_{H,H} = 6.4 Hz), 0.20 (s, CH₂SiMe₃, 9H). It was also observed that ~0.33 eq. of 2,4,6-triphenyl triazine was also generated along with the ketimide product, as determined by its characteristic ¹H NMR resonances. ¹H NMR (300 MHz, C₆D₆): δ 8.85 (m, CH_{Ar}, 6H), 7.31 (m, CH_{Ar}, 9H).

Generation of Th(NH-2,6-*i*Pr₂-C₆H₃)(BIMA)₃ (9**):** Solid **1** (0.020 g, 0.027 mmol) was added to a 4 mL dram vial and dissolved in C₆D₆ (0.3 mL). In a separate dram vial, 2,6-diisopropylaniline (0.005 g, 0.028 mmol) was weighed out and dissolved in C₆D₆ (0.3 mL). The two solutions were then combined and added to a *J*-Young NMR tube sealed with a Teflon screw cap. The solution was then heated at 100 °C for 5 d, resulting in >90% conversion to **9** as judged by ¹H NMR spectroscopy. ¹H NMR (300 MHz, C₆D₆): δ 7.25 (d, CH_{Ar}, 2H, ³J_{H,H} = 7.5 Hz), 6.91 (t, CH_{Ar}, 1H, ³J_{H,H} = 7.5 Hz), 4.94 (brs, NH, 1H), 3.65 (sept, CHMe₂, 6H, ³J_{H,H} = 6.5 Hz), 3.54 (sept, CHMe₂, 2H, ³J_{H,H} = 6.7 Hz), 1.70 (s, NC(CH₃)N, 9H), 1.42 (d, CHMe₂, 12H, ³J_{H,H} = 6.7 Hz), 1.17 (d, CHMe₂, 36H, ³J_{H,H} = 6.5 Hz).

Generation of Th(O-2,6-*t*Bu₂-C₆H₃)(BIMA)₃ (10**):** Solid **1** (0.021 g, 0.028 mmol) was added to a 4 mL dram vial and dissolved in C₆D₆ (0.3 mL). In a separate dram vial, 2,6-di-*tert*-butylphenol (0.006 g, 0.029 mmol) was weighed out and dissolved in C₆D₆ (0.3 mL). The two solutions were then combined and added to a *J*-Young NMR tube sealed with a Teflon screw cap. The solution was allowed to stand at ambient temperature for 12 h, at which point full conversion to **10** had been achieved as judged by ¹H NMR spectroscopy. ¹H NMR (600 MHz, C₆D₆): δ 7.40 (d, CH_{Ar}, 2H, ³J_{H,H} = 7.7 Hz), 6.85 (t, CH_{Ar}, 1H, ³J_{H,H} = 7.7 Hz), 3.71 (sept, CHMe₂, 6H, ³J_{H,H} = 6.5 Hz), 1.74 (s, NC(CH₃)N, 9H), 1.73 (s, C(CH₃)₃, 18H), 1.20 (d, CHMe₂, 36H, ³J_{H,H} = 6.5 Hz).

Synthesis of Th(PHMe)(BIMA)₃ (11a**):** Solid ThCl(BIMA)₃ (0.243 g, 0.352 mmol) was added to a 20 mL scintillation vial containing a magnetic stir bar and dissolved in diethyl ether (2 mL). To this stirred solution was added KPHMe (0.082 g, 0.431 mmol) in THF (2 mL) dropwise, resulting in a light orange/yellow, cloudy solution. The reaction was allowed to stir at room temperature for 48 h, at which point the reaction appeared bright yellow. The volatiles were removed under reduced pressure, and the resulting solid was triturated with hexanes (2 x 2 mL), extracted into pentane (6 mL), filtered through Celite and concentrated to ~1.5 mL. The solution was then placed in the freezer at -35 °C for 16 h, resulting in yellow crystals of **11a** (0.164 g, 57.8%) ¹H NMR (600 MHz, C₆D₆): δ 7.01 (s, CH_{Ar}, 2H), 3.60 (sept, CHMe₂, 6H, ³J_{H,H} = 6.4 Hz), 3.42 (d, PH, ¹J_{P,H} = 195 Hz, 1H), 2.74 (s, *o*-CH₃, 6H), 2.42 (s, *p*-CH₃, 3H), 1.63 (s, NC(CH₃)N, 9H), 1.22 (d, CHMe₂, 36H, ³J_{H,H} = 6.4 Hz). ¹³C{¹H} (151 MHz, C₆D₆): δ 174.3 (NCN), 147.5 (d, C_{Ar,ipso}, ¹J_{P,C} = 35.2 Hz), 137.5 (d, C_{Ar,o}, ²J_{P,C} = 9.1 Hz), 129.9 (C_{Ar,p}), 127.7 (d, C_{Ar,m}, ³J_{P,C} = 2.7 Hz), 48.8 (CHMe₂), 25.7 (d, H₃C_{Ar,o}, ¹SJ_{P,C} = 9.6 Hz), 24.7 (d, CHMe₂, ¹SJ_{P,C} = 2.1 Hz), 21.0 (H₃C_{Ar,p}), 13.9 (NC(CH₃)N). ³¹P NMR (162 MHz, C₆D₆): δ -45.4 (d, ¹J_{P,H} = 195 Hz). Anal. Calcd for C₃₃H₆₃N₆PTh (806.9): C, 49.12; H, 7.87; N, 10.42. Found: C, 48.79; H, 7.85; N, 10.36. Mp: 102(2) °C. FTIR (Nujol): 2337 (w, ν_{P-H}), 1337 (m), 1314 (m), 1196 (m),

1174 (w), 1122 (w), 1056 (w), 1013 (w), 847 (w), 806 (w), 722 (m), 620 (w). Crystals suitable for single-crystal X-ray diffraction studies were grown from a concentrated pentane solution stored at -35 °C for 16 h.

Generation of Th(PPh₂)(BIMA)₃ (11b): Solid **1** (0.021 g, 0.028 mmol) was added to a 4 mL dram vial and dissolved in C₆D₆ (0.3 mL). In a separate dram vial, PPh₂ (0.0052 g, 0.028 mmol) was weighed out and dissolved in C₆D₆ (0.3 mL). The two solutions were then combined and added to a *J*-Young NMR tube sealed with a Teflon screw cap. The solution was then heated at 100 °C for 4 d, resulting in a bright orange solution and >95% conversion to **11b** as judged by ¹H NMR spectroscopy. ¹H NMR (600 MHz, C₆D₆): δ 7.81 (m, CH_{Ar}, 4H), 7.22 (m, CH_{Ar}, 4H), 6.96 (m, CH_{Ar}, 2H), 3.60 (sept, CHMe₂, 6H, ³J_{H,H} = 6.4 Hz), 1.63 (s, NC(CH₃)N, 9H), 1.20 (d, CHMe₂, 36H, ³J_{H,H} = 6.4 Hz). ³¹P{¹H} NMR (162 MHz, C₆D₆): δ 89.5. It was also observed that the dehydrocoupled product, Ph₂P-PPh₂, was generated in small quantities as determined by its characteristic ³¹P NMR resonance in C₆D₆ (δ -14.9) as well as an unidentified phosphorus-containing species (³¹P: δ 106). Synthesis of **11a** via protonolysis of **1** with mesitylphosphine followed identical reaction conditions.

Synthesis of Th(C≡C-*p*-tolyl)(BIMA)₃ (12): Solid **1** (0.400 g, 0.538 mmol) was added to a 20 mL scintillation vial containing a magnetic stir bar and dissolved in hexanes (10 mL). To this stirred solution was added neat *p*-tolylacetylene (0.065 g, 0.560 mmol) dropwise, resulting in a faint yellow solution which was allowed to stir at ambient temperature for 1 h. The volatiles were removed under reduced pressure, and the resulting solid was extracted into hexanes (10 mL), concentrated to 6 mL, and placed in the freezer at -35 °C for 16 h, resulting in colourless crystals of **12** (0.392 g, 94.5%). ¹H NMR (600 MHz, C₆D₆): δ 7.69 (d, CH_{ptolyl}, 2H, ³J_{H,H} = 8.0 Hz), 6.96 (d, CH_{ptolyl}, 2H, ³J_{H,H} = 8.0 Hz), 3.66 (sept, CHMe₂, 6H, ³J_{H,H} = 6.3 Hz), 2.04 (s, CH_{3,ptolyl}, 3H), 1.66 (s, NC(CH₃)N, 9H), 1.42 (d, CHMe₂, 36H, ³J_{H,H} = 6.3 Hz). ¹³C{¹H} NMR (151 MHz, C₆D₆): δ 189.2 (ThC≡C), 172.7 (NCN), 134.9 (C_{ptolyl}), 131.0 (C_{ptolyl}), 128.8 (C_{ptolyl}), 124.7 (C_{ptolyl}), 107.8 (ThC≡C), 48.3 (CHMe₂), 24.6 (CHMe₂), 20.9 (C₆H₄Me), 11.8 (NC(CH₃)N). Anal. Calcd for C₃₃H₅₈N₆Th (770.9): C, 51.42; H, 7.58; N, 10.90. Found: C, 51.72; H, 7.55; N, 10.60. Mp: 131(2) °C. FTIR (Nujol): 2599 (w), 2061 (w, ν_{C=C}), 1358 (s), 1332 (s), 1313 (s), 1198 (s), 1173 (s), 1137 (w), 1125 (m), 1051 (w), 1016 (m), 819 (s), 803 (s), 711 (w), 618 (w), 569 (w), 546 (w), 534 (w), 464 (m). Crystals suitable for single-crystal X-ray diffraction studies were grown from a concentrated hexanes solution stored at -35 °C for 16 h.

Synthesis of Th[(THF)(BIMA)₃][BPh₄] (13): Solid **1** (0.300 g, 0.404 mmol) was added to a 20 mL scintillation vial containing a magnetic stir bar and dissolved in THF (4 mL). To this stirred solution was added a THF solution (2 mL) of [Et₃NH][BPh₄] (0.170 g, 0.403 mmol), and the resulting colourless solution was allowed to stir at ambient temperature for 2 h. The volatiles were removed under reduced pressure, and the resulting solid was re-dissolved in THF (6 mL), concentrated to 2 mL, and placed in the freezer at -35 °C for 16 h, resulting in colourless crystals of **13** (0.368 g, 81.4%). The complex crystallizes with an equivalent of THF in the lattice, which can be removed under vacuum. ¹H NMR (600 MHz, CDCl₃): δ 7.43 (br s, CH_{Ar}, 8H), 7.06 (m, CH_{Ar}, 8H), 6.91 (m, CH_{Ar}, 4H), 3.94 (m, ^{THF}CH₂, 4H), 3.84 (sept, CHMe₂, 6H, ³J_{H,H} = 6.4 Hz), 2.02 (s, NC(CH₃)N, 9H), 1.91 (m, ^{THF}CH₂, 4H), 1.16 (d, CHMe₂, 36H, ³J_{H,H} = 6.4 Hz). ¹¹B{¹H}

NMR (192 MHz, CDCl₃): -7.16 (s). ¹³C{¹H} (151 MHz, CDCl₃): δ 176.4 (NCN), 164.4 (B-C_{Ph}, ¹J_{B,C} = 49.7 Hz), 136.4 (C_{Ph}), 125.5 (C_{Ph}), 121.6 (C_{Ph}), 69.6 (^{THF}CH₂), 48.7 (CHMe₂), 25.6 (^{THF}CH₂), 25.2 (CHMe₂), 14.0 (NC(CH₃)N). Anal. Calcd for C₅₂H₇₈N₆O₁B₁Th (1046.1): C, 59.71; H, 7.52; N, 8.03. Found: C, 59.38; H, 7.53; N, 8.21. Mp: 183(5) °C. FTIR (Nujol): 1378 (s), 1345 (m), 1315 (m), 1194 (m), 1174 (w), 1124 (w), 1015 (w), 806 (w), 742 (w), 730 (m), 706 (m), 614 (w), 605 (w), 424 (w). Crystals suitable for single-crystal X-ray diffraction studies were grown from a concentrated THF solution stored at -35 °C for 16 h.

Synthesis of (BIMA)₃Th(μ-H)₂[B(C₈H₁₄)] (14): Solid **1** (0.251 g, 0.338 mmol) was added to a 20 mL scintillation vial containing a magnetic stir bar and dissolved in 2 mL toluene. To this stirred solution was added a toluene solution (3 mL) of 9-BBN dimer (0.082 g, 0.336 mmol) dropwise over 1 minute. The resulting colourless solution was allowed to stir at ambient temperature for 48 h. The volatiles were removed under reduced pressure, and the resulting solid was triturated with hexane (2 x 4 mL) and extracted into HMDSO (8 mL), leaving behind a small amount of insoluble, colourless solid. The HMDSO extract was then filtered through Celite, concentrated to 5 mL, and placed in the freezer at -35 °C for 16 h, resulting in colourless crystals of **14** (0.173 g, 65.8%). ¹H NMR (300 MHz, C₆D₆): δ 4.67-5.30 (br, μ-H, 2H), 3.68 (sept, CHMe₂, 6H, ³J_{H,H} = 6.5 Hz), 2.25-2.41 (m, BBN, 10H), 2.06 (m, BBN, 2H), 1.78 (brs, BBN, 2H), 1.66 (s, NC(CH₃)N, 9H), 1.23 (d, CHMe₂, 36H, ³J_{H,H} = 6.5 Hz). ¹¹B{¹H} NMR (192 MHz, C₆D₆): δ 4.90 (s). ¹³C{¹H} (126 MHz, C₆D₆): δ 174.6 (NCN), 48.7 (CHMe₂), 34.5 (BBN), 25.8 (BBN), 24.7 (CHMe₂), 14.6 (NC(CH₃)N). Anal. Calcd for C₃₂H₆₇BN₆Th (778.8): C, 49.35; H, 8.67; N, 10.79. Found: C, 49.30; H, 8.59; N, 10.68; Mp: 207(2) °C. FTIR (Nujol): 2021 cm⁻¹ (br, B-H), 1377 (s), 1334 (s), 1313 (s), 1283 (s), 1197 (s), 1171 (s), 1119 (m), 1051 (m), 1011 (m), 919 (w), 805 (m), 775 (w), 723 (m), 618 (w), 575 (w), 543 (w). Crystals suitable for single-crystal X-ray diffraction studies were grown from a concentrated pentane solution stored at -35 °C for 16 h.

Synthesis of Th(BIMA)₂(BIMA*) (15): Solid **1** (0.500 g, 0.673 mmol) was added to a 4 mL dram vial and dissolved in 1.5 mL C₆D₆. The solution was transferred to a *J*-Young NMR tube and sealed with a Teflon screw cap. The *J*-Young tube was then placed in the photolysis reactor and irradiated for 10 days, at which point the solution had changed from colourless to green, and **1** was completely consumed as observed by ¹H NMR spectroscopy. The *J*-Young tube was then brought into the glovebox and emptied into a 20 mL scintillation vial, and the tube was rinsed with toluene (2 mL). This rinse was combined with the C₆D₆ solution, and the volatiles were then removed under reduced pressure. The resulting solid was then extracted into toluene (4 mL), concentrated to 1 mL and placed in the freezer at -35 °C for 16 h, resulting in colourless crystals of **15** (0.232 g, 52.7%). ¹H NMR (600 MHz, C₆D₆): δ 4.24 (sept, CHMe₂*, 2H, ³J_{H,H} = 6.2 Hz), 3.57 (sept, CHMe₂, 4H, ³J_{H,H} = 6.2 Hz), 3.44 (s, NC(CH₂)N*, 2H), 1.54 (d, CHMe₂*, 12H, ³J_{H,H} = 6.2 Hz), 1.53 (s, NC(CH₃)N, 6H), 1.15 (d, CHMe₂, 24H, ³J_{H,H} = 6.2 Hz). ¹³C{¹H} NMR (151 MHz, C₆D₆): δ 172.8 (NCN), 154.2 (NCN*), 53.3 (NC(CH₂)N*), 49.1 (Me₂CH*), 48.3 (Me₂CH), 26.0 (Me₂CH*), 25.7 (Me₂CH), 12.2 (NC(CH₃)N). Anal. Calcd for C₂₄H₅₀N₆Th (654.7): C, 44.03; H, 7.70; N, 12.84. Found: C, 43.77; H, 7.67; N, 12.46. Mp: 170(decomp.) °C. FTIR (Nujol): 1496 (s), 1414 (s), 1308 (s), 1197 (s), 1169 (m), 1123 (m), 1049 (m), 1010 (m), 886 (w), 796 (s), 722 (w), 695 (m), 620 (w), 577 (w), 546 (w), 456 (w), 433 (w). Crystals

suitable for single-crystal X-ray diffraction studies were grown from a concentrated toluene solution stored at -35 °C for 16 h. Alternatively, solid **1** (0.009 g, 0.012 mmol) was added to a 4 mL dram vial and dissolved in 0.4 mL C₆D₁₂. The solution was transferred to a quartz EPR tube custom-fitted with a *J*-Young neck and sealed with a Teflon screw cap. The tube was then placed in front of a xenon arc lamp and irradiated for 2 h, at which point the solution had changed from colourless to green, and **1** was completely consumed as observed by ¹H NMR spectroscopy.

B. NMR Spectroscopic Data

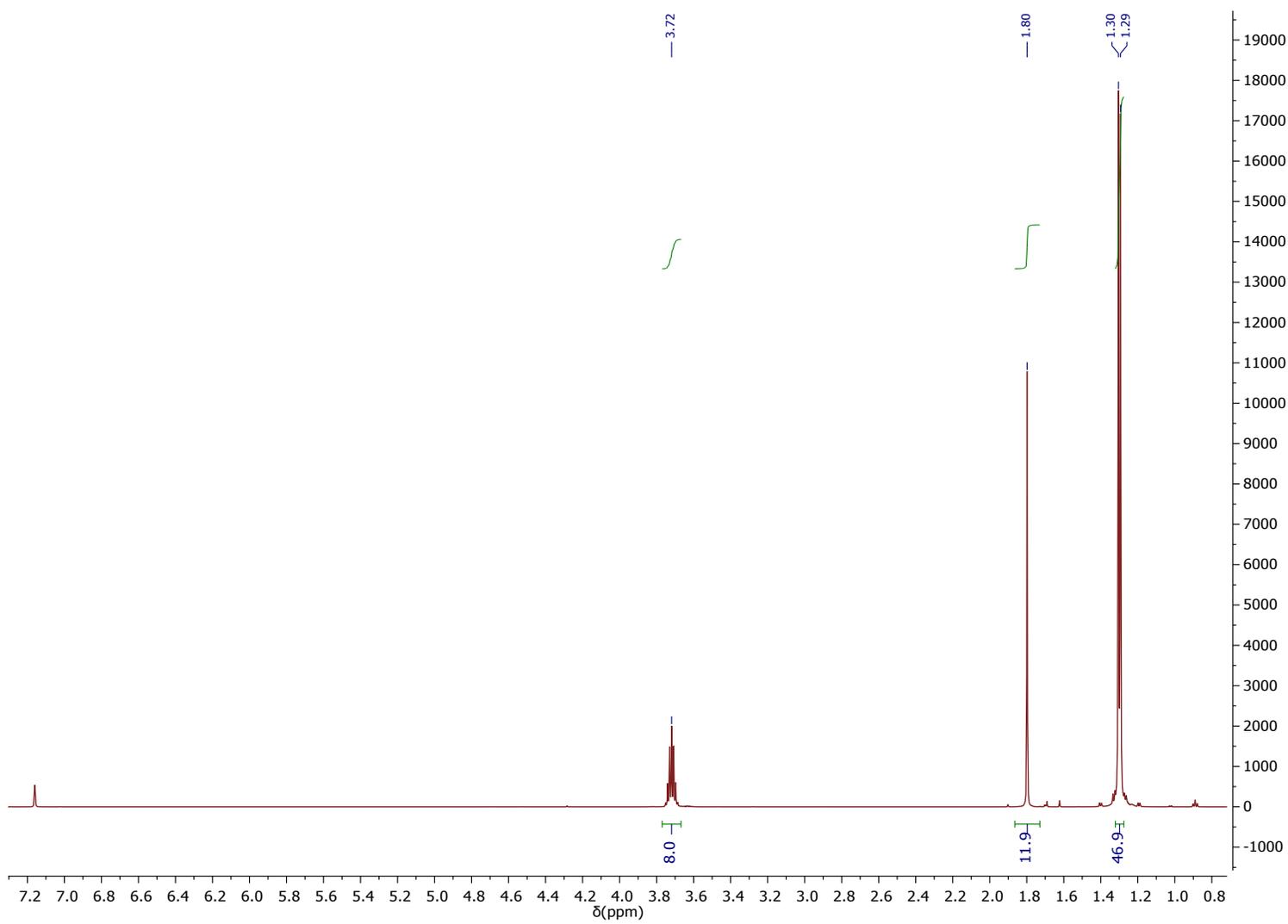


Figure S1. ^1H NMR spectrum of $\text{Th}(\text{BIMA})_4$ (**2**) at 298 K in C_6D_6

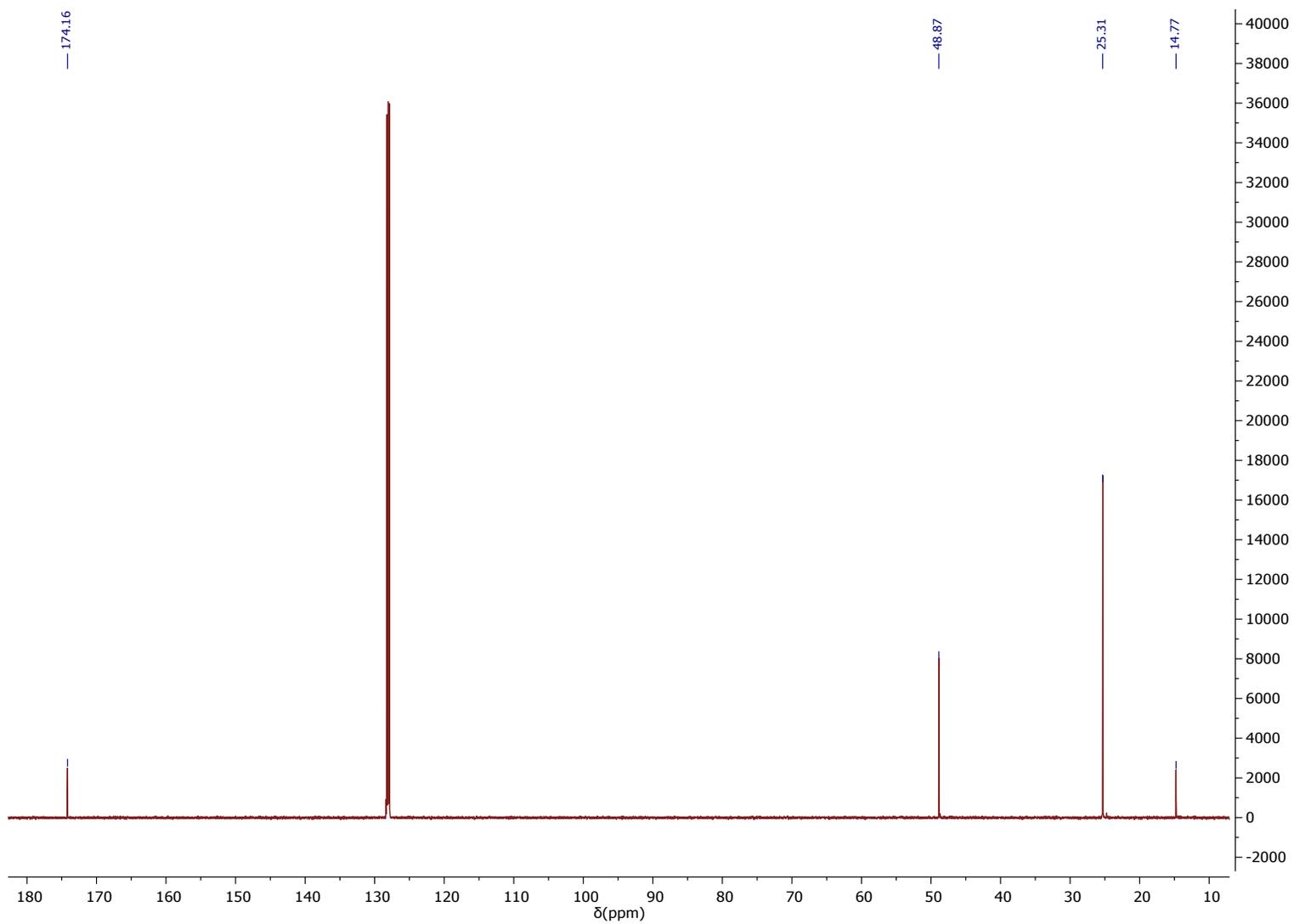


Figure S2. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{Th}(\text{BIMA})_4$ (2) at 298 K in C_6D_6

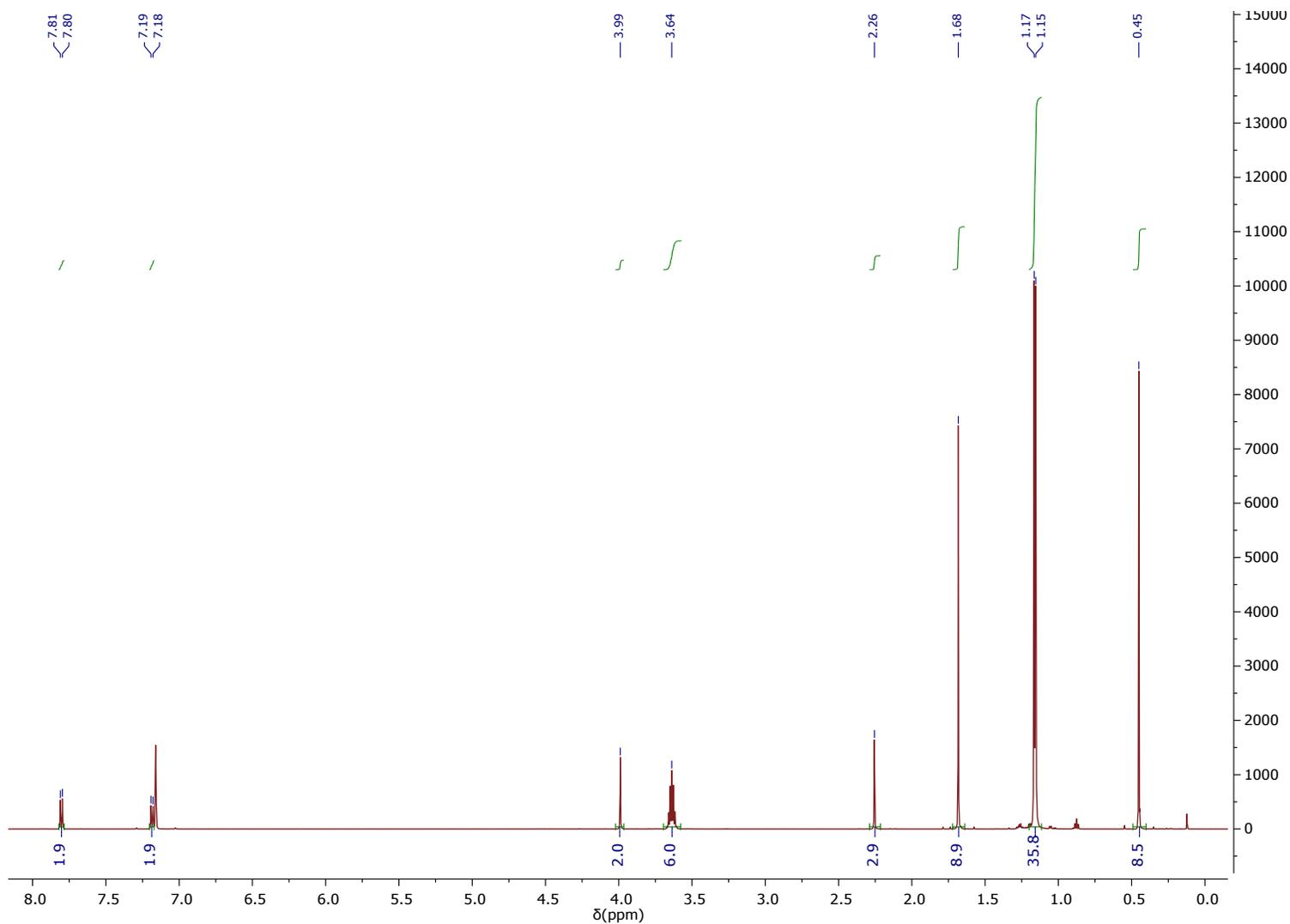


Figure S3. ¹H NMR spectrum of Th[(*p*-tolyl)NNN(CH₂SiMe₃)-κ²N^{1,2}](BIMA)₃ (**3**) at 298 K in C₆D₆

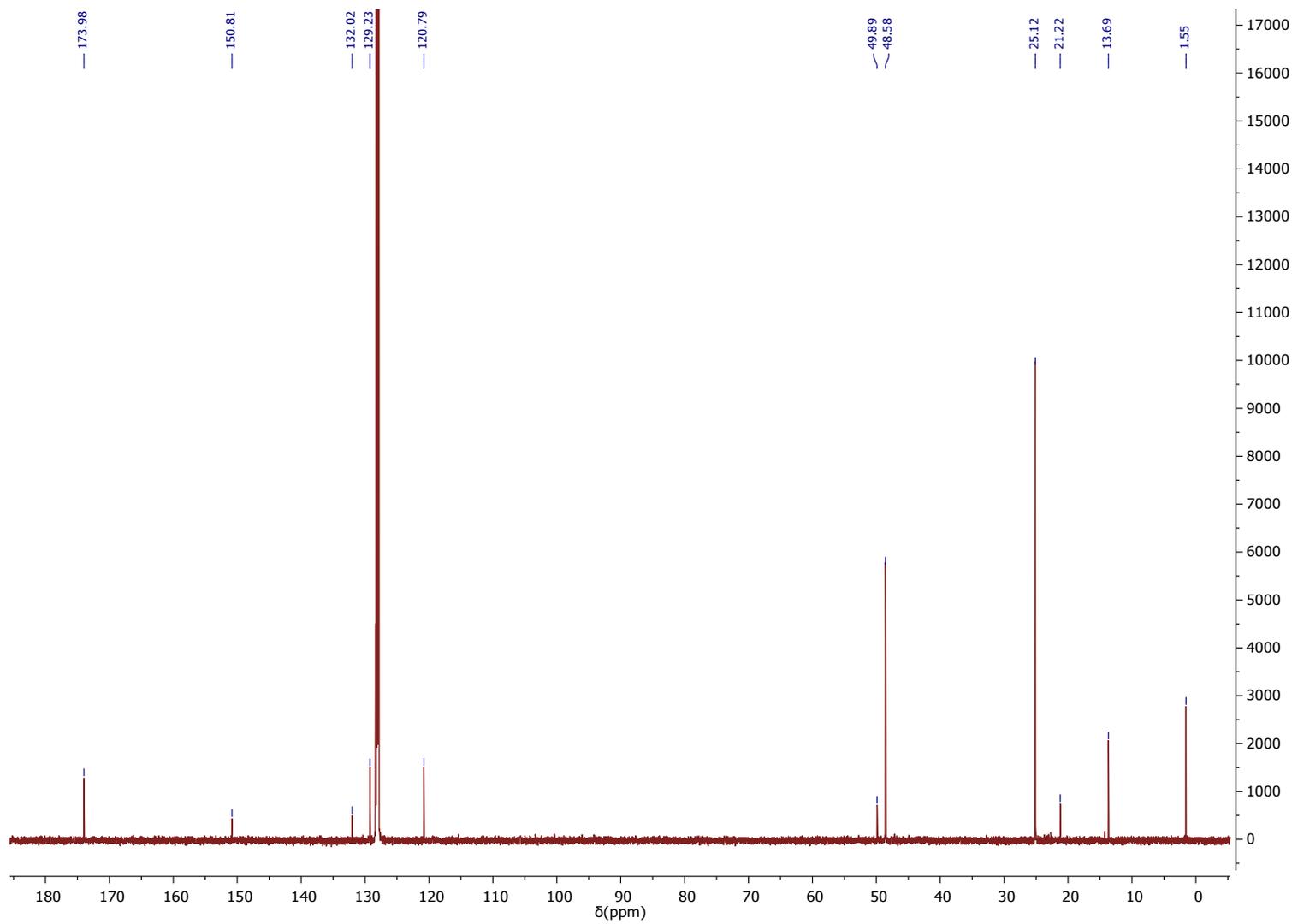


Figure S4. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{Th}[(p\text{-tolyl})\text{NNN}(\text{CH}_2\text{SiMe}_3)\text{-}\kappa^2\text{N}^{1,2}](\text{BIMA})_3$ (**3**) at 298 K in C_6D_6

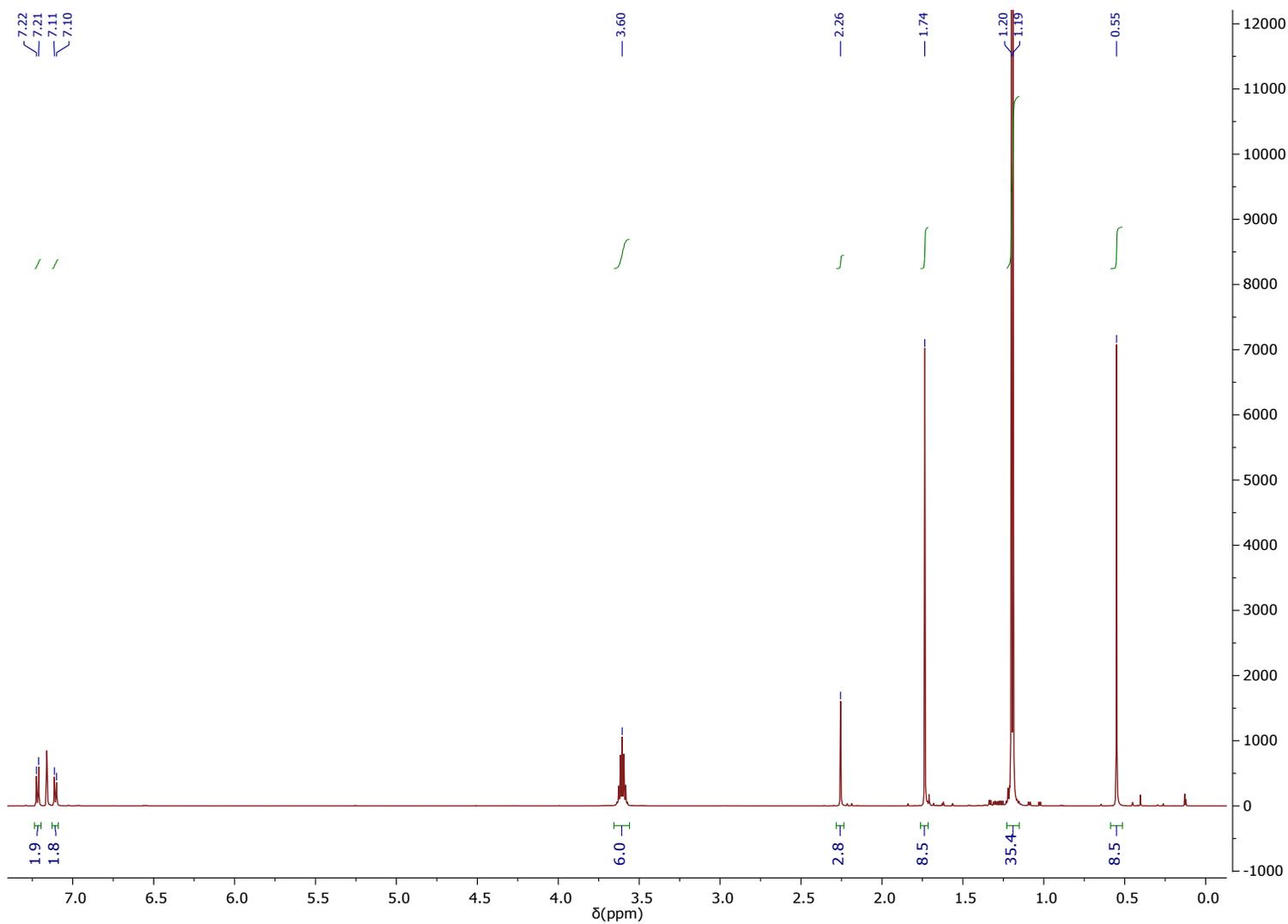


Figure S5. ^1H NMR spectrum of $\text{Th}[(p\text{-tolyl})\text{N}(\text{SiMe}_3)](\text{BIMA})_3$ (**4**) at 298 K in C_6D_6

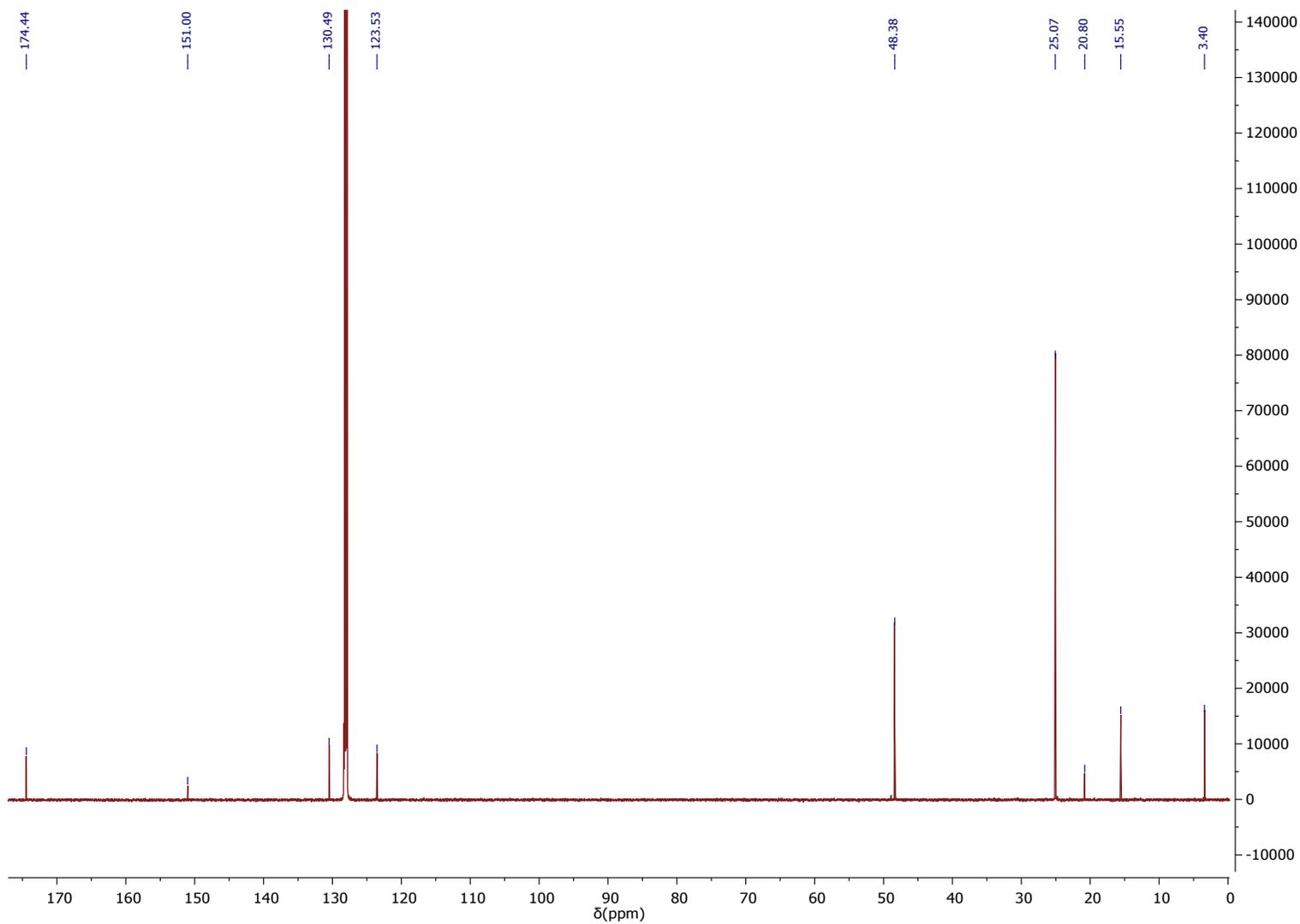


Figure S6. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{Th}[(p\text{-tolyl})\text{N}(\text{SiMe}_3)](\text{BIMA})_3$ (4) at 298 K in C_6D_6

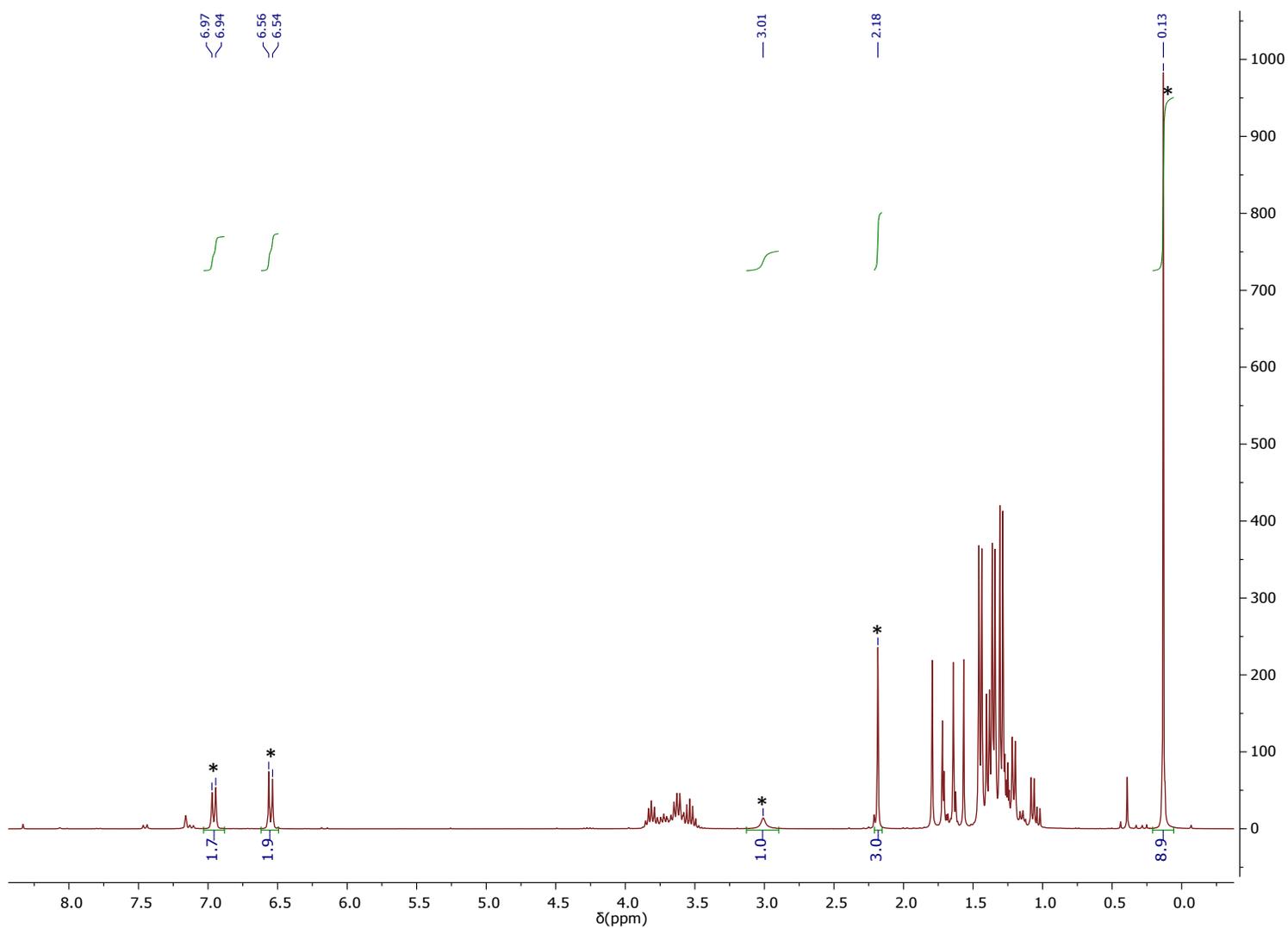


Figure S7. ¹H NMR spectrum of **3** (0.100 g, 0.114 mmol) in 0.6 mL C₆D₆ after heating at 70 °C for 4 d.
*Resonances attributable to (*p*-tolyl)NH(SiMe₃)

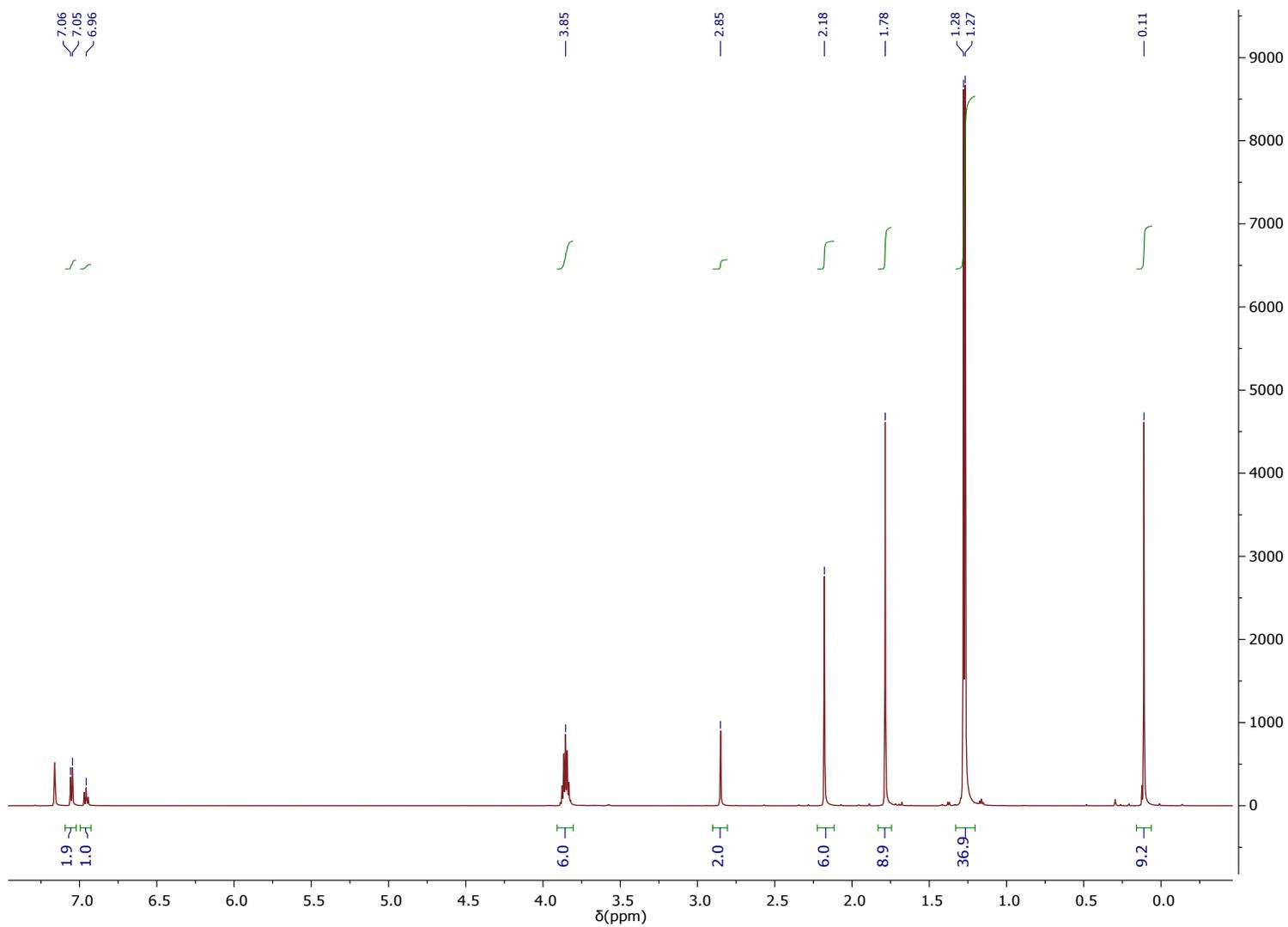


Figure S8. ¹H NMR spectrum of Th[η^2 -(C=N)-2,6-Me₂-C₆H₃(CH₂SiMe₃)](BIMA)₃ (**5**) at 298 K in C₆D₆

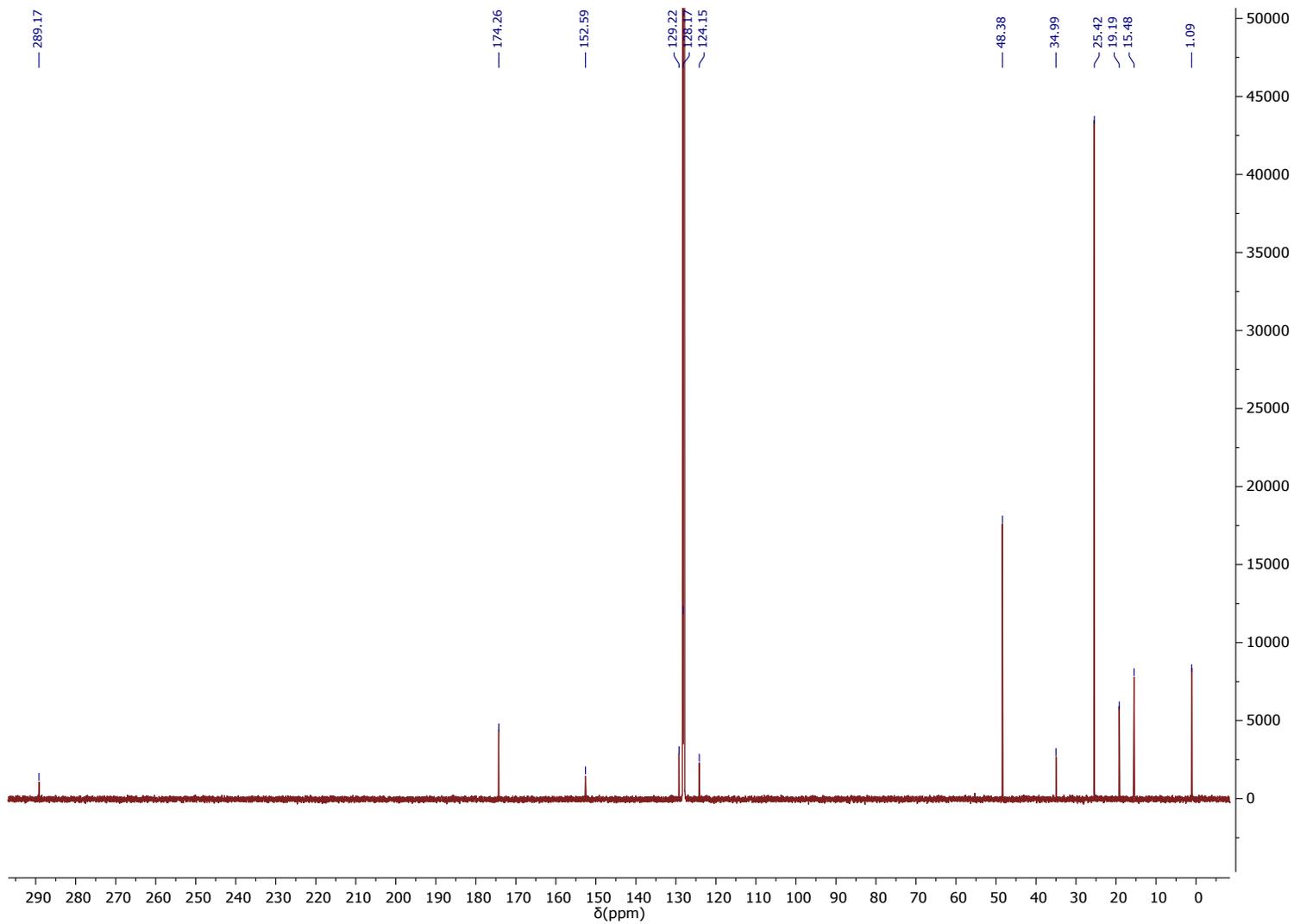


Figure S9. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{Th}[\eta^2\text{-(C=N)-2,6-Me}_2\text{-C}_6\text{H}_3(\text{CH}_2\text{SiMe}_3)](\text{BIMA})_3$ (**5**) at 298 K in C_6D_6

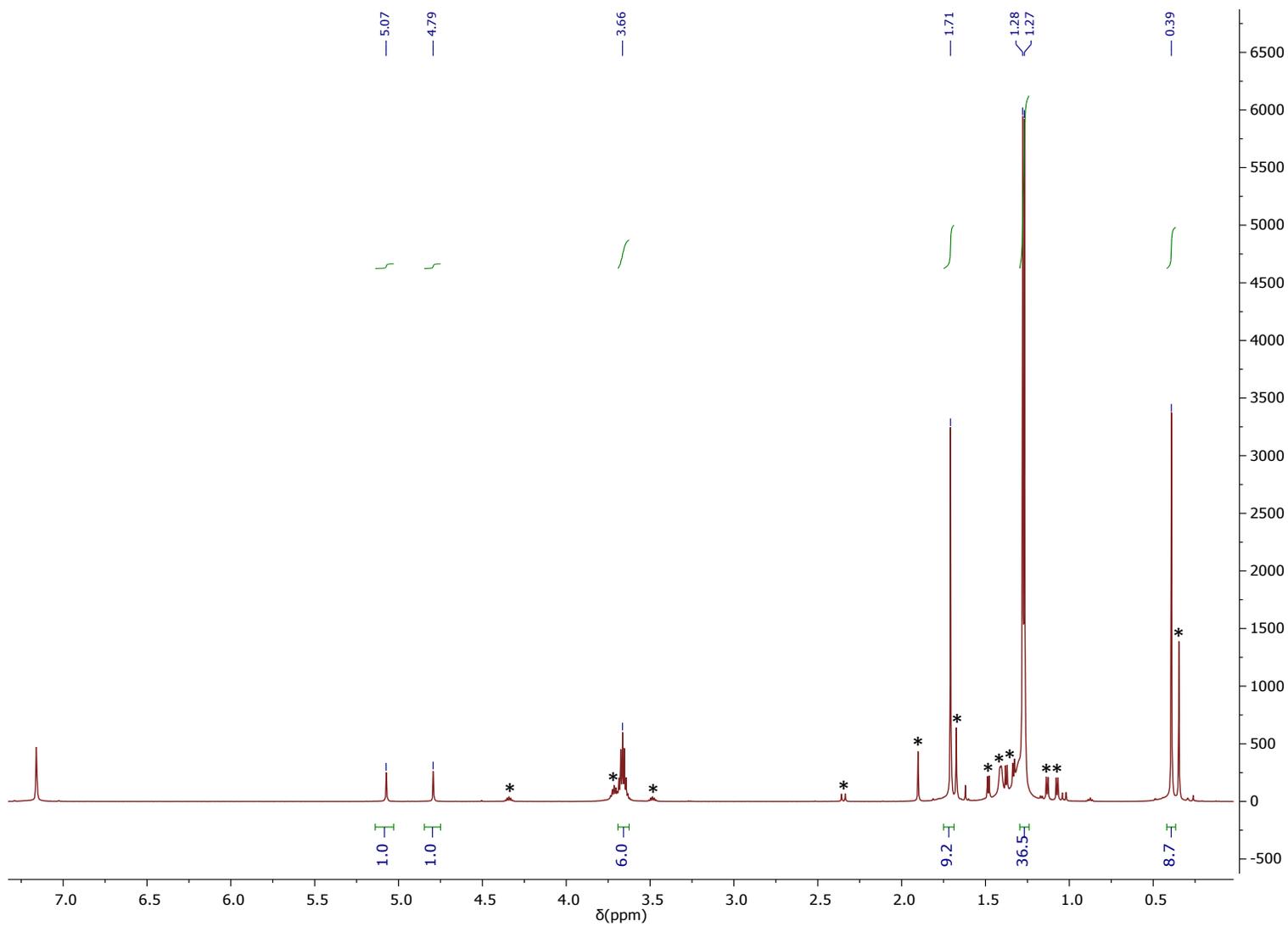


Figure S10. ^1H NMR spectrum of bulk mixture of **6** and **7** at 298 K in C_6D_6 . Integrated resonances are attributable to **6**. *Resonances attributable to **7**

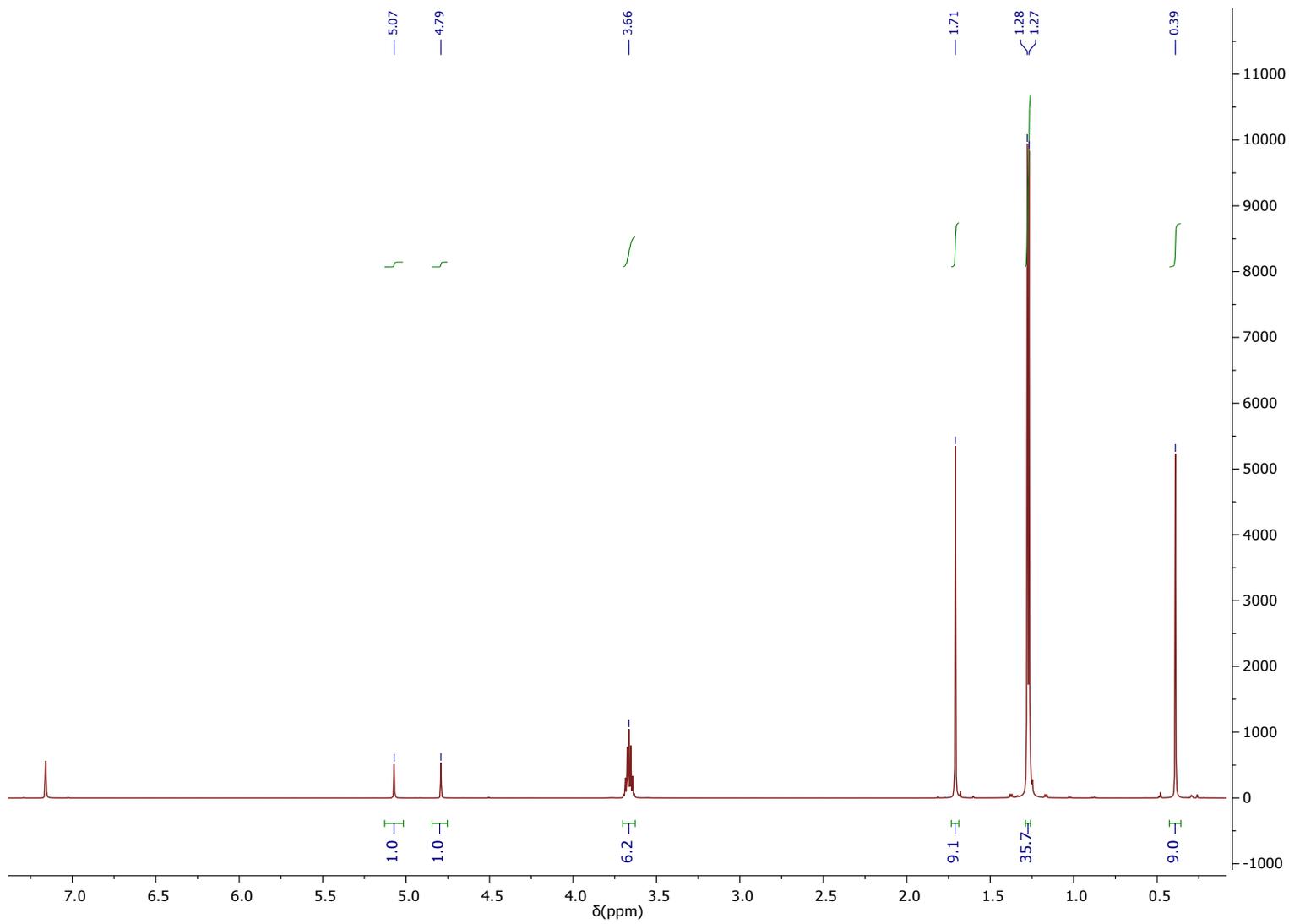


Figure S11. ^1H NMR spectrum of $\text{Th}[\text{OC}(=\text{CH}_2)\text{SiMe}_3](\text{BIMA})_3$ (**6**) at 298 K in C_6D_6

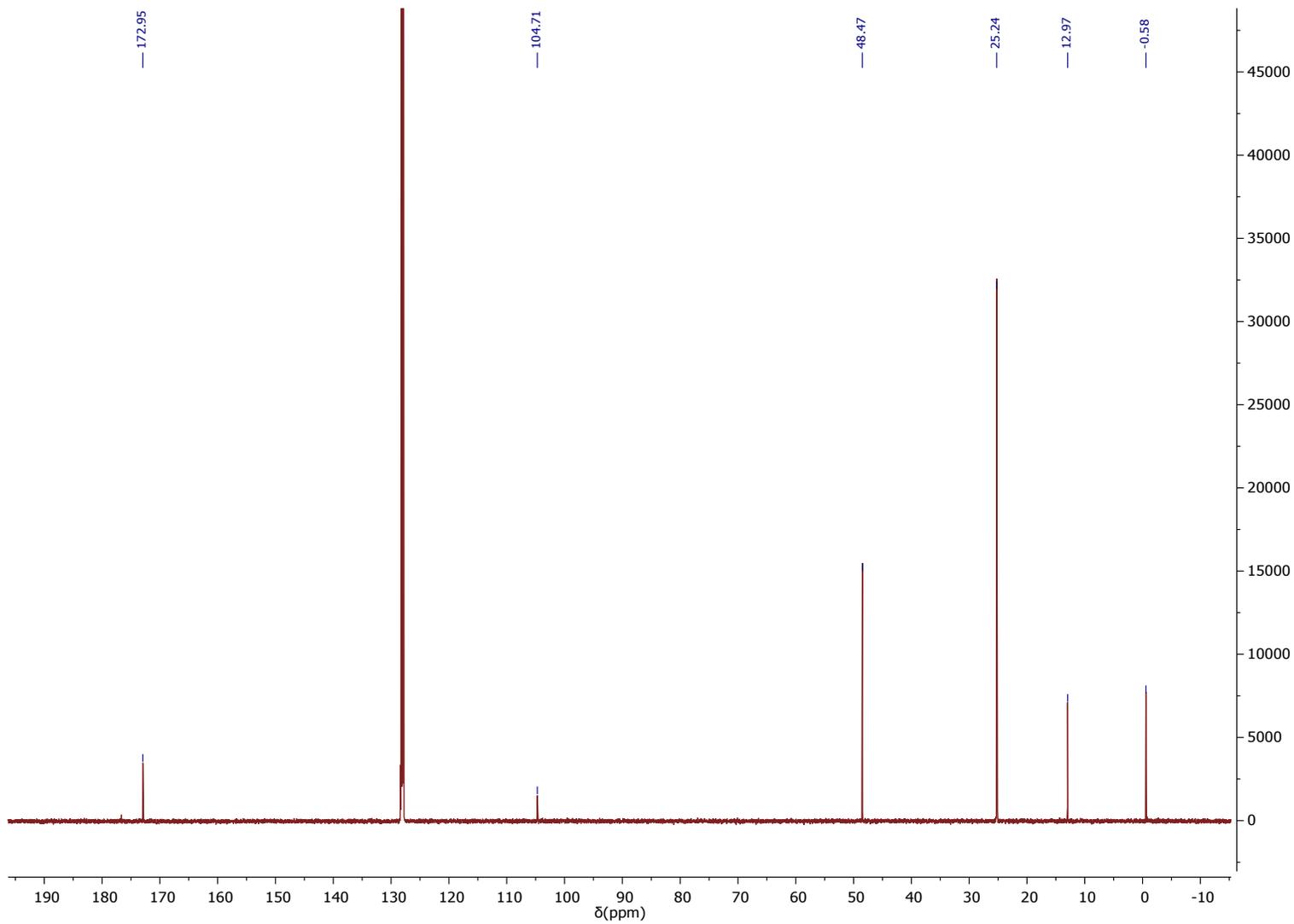


Figure S12. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{Th}[\text{OC}(=\text{CH}_2)\text{SiMe}_3](\text{BIMA})_3$ (**6**) at 298 K in C_6D_6

S19

S20

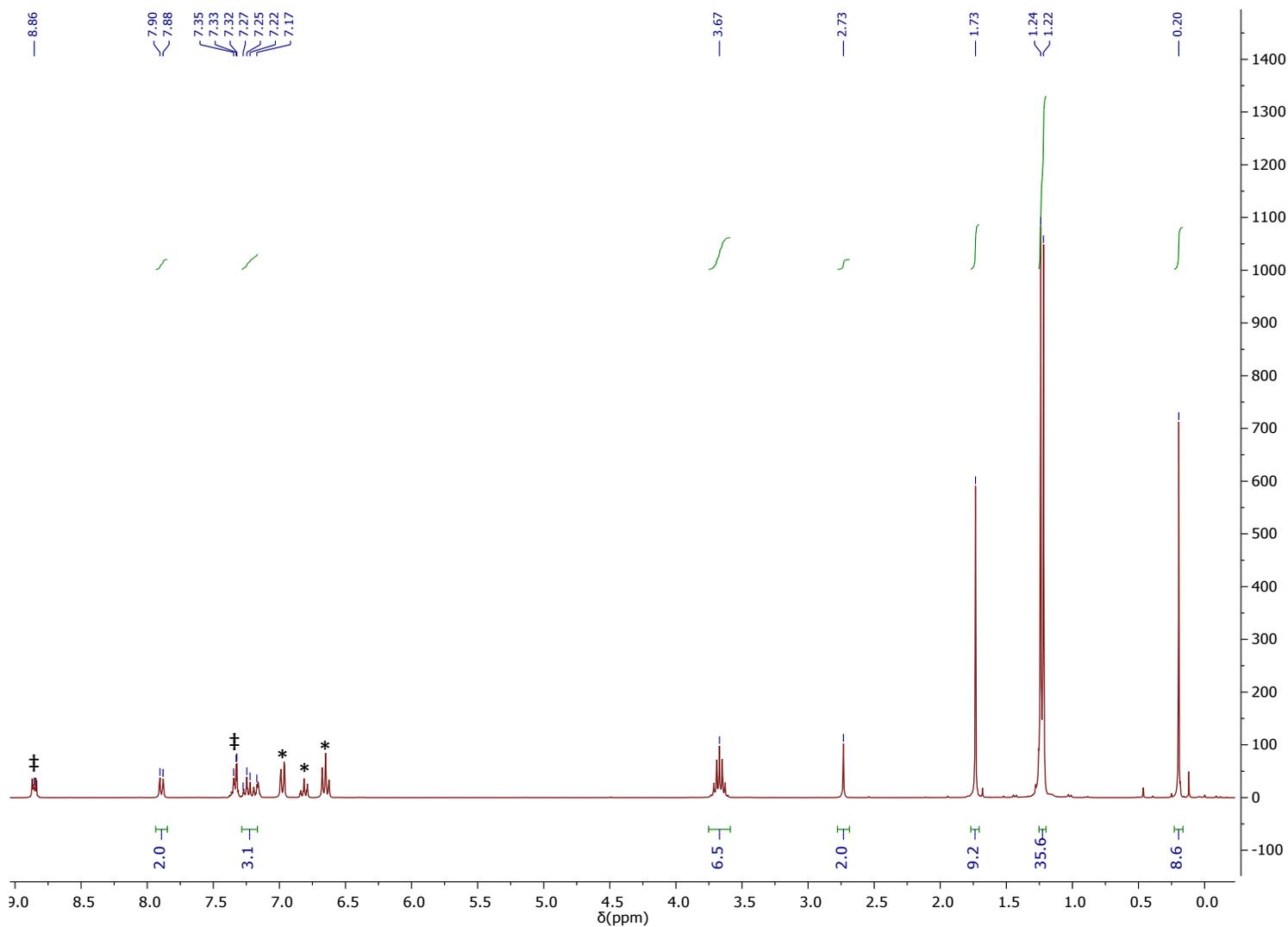


Figure S13. ^1H NMR spectrum of $\text{Th}[-\text{N}=\text{C}(\text{Ph})(\text{CH}_2\text{SiMe}_3)](\text{BIMA})_3$ (**8**) generated *in situ*, at 298 K in C_6D_6 . †PhCN. ‡2,4,6-triphenyl triazine

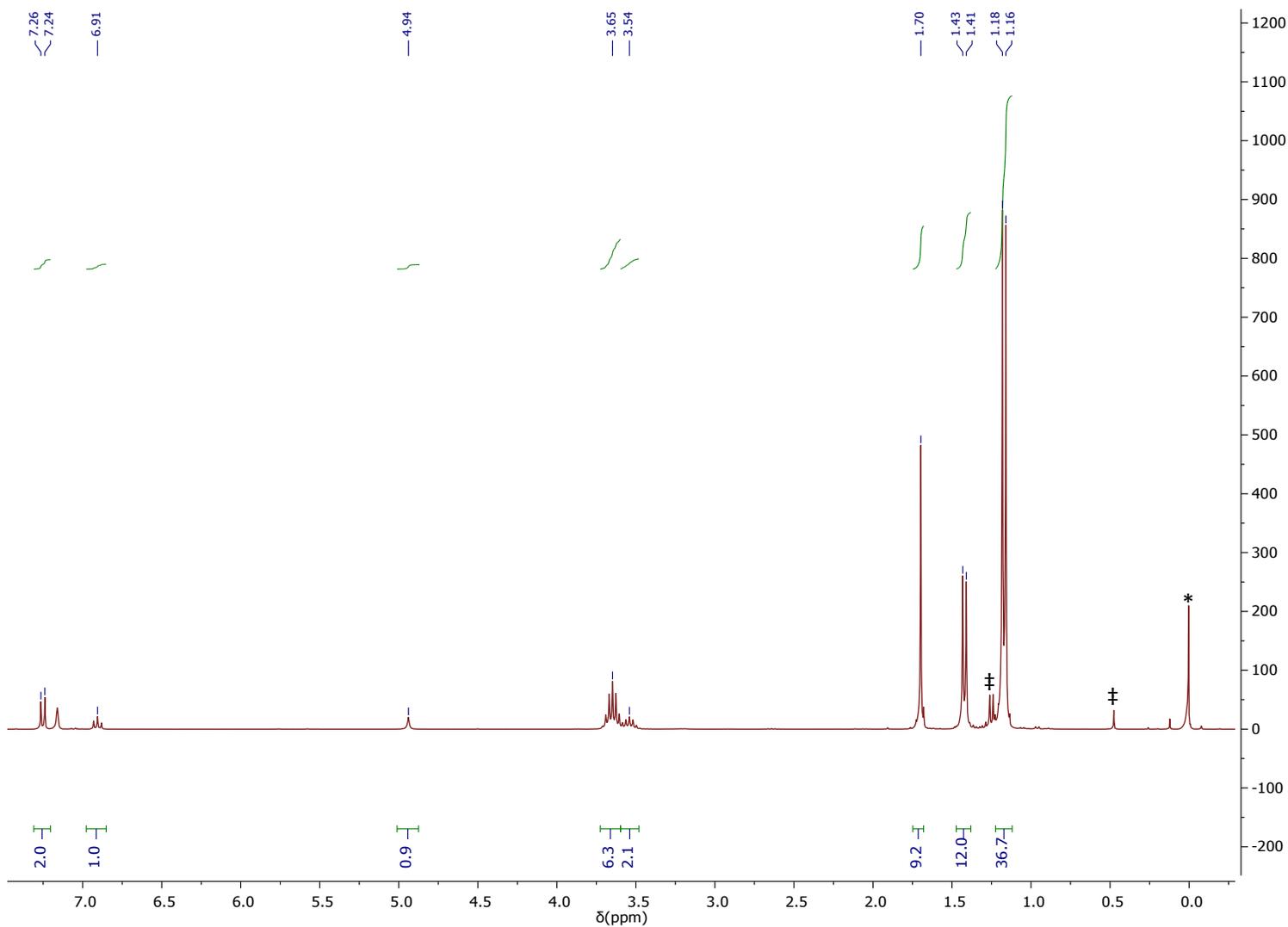


Figure S14. ^1H NMR spectrum of $\text{Th}(\text{NH-2,6-}i\text{Pr}_2\text{-C}_6\text{H}_3)(\text{BIMA})_3$ (**9**) generated *in situ*, at 298 K in C_6D_6 . * SiMe_4 . †1

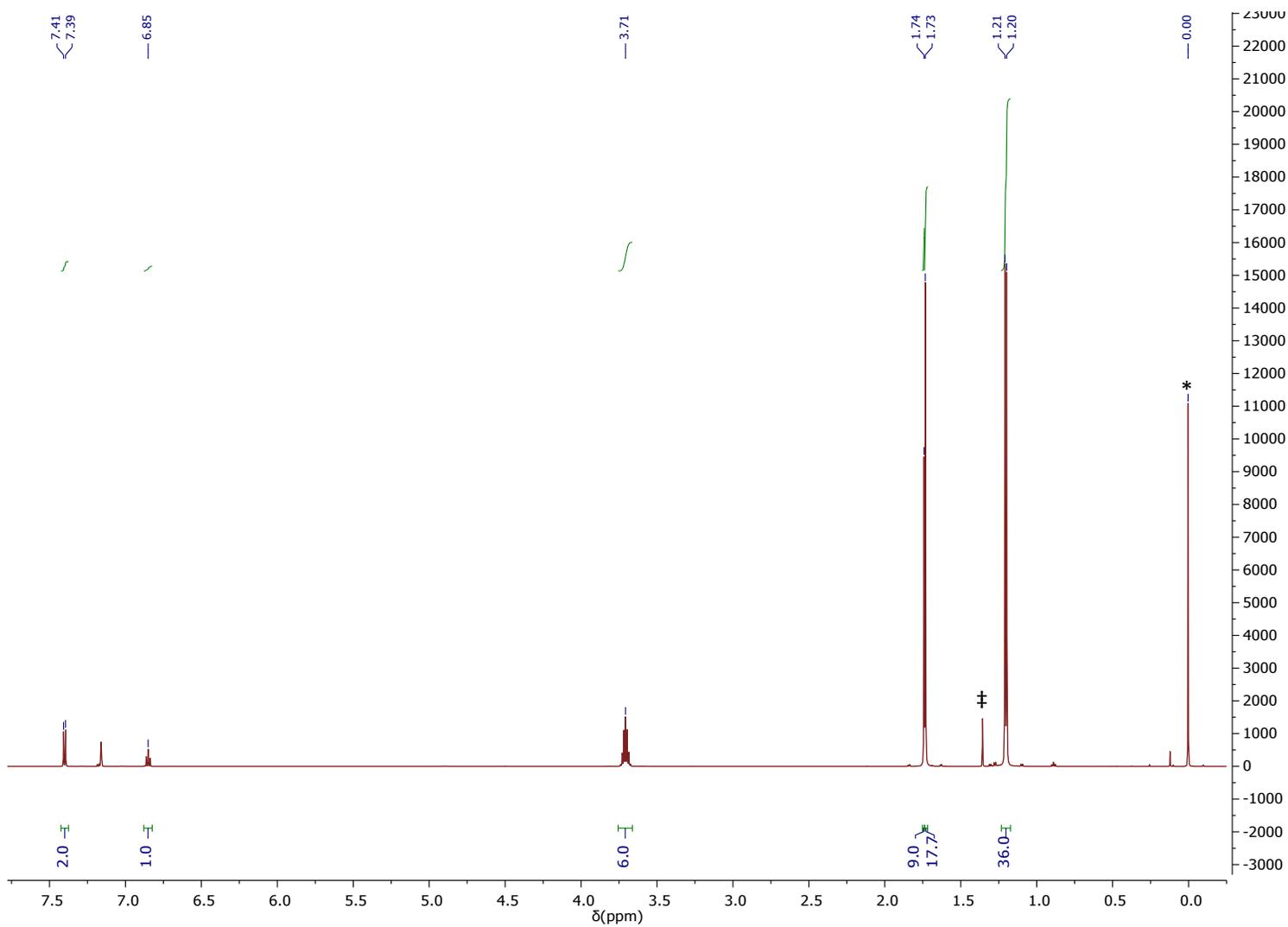


Figure S15. ^1H NMR spectrum of $\text{Th}(\text{O}-2,6\text{-}t\text{-Bu}_2\text{-C}_6\text{H}_3)(\text{BIMA})_3$ (**10**) generated *in situ*, at 298 K in C_6D_6 . * SiMe_4 . †2,6-di-*tert*-butylphenol

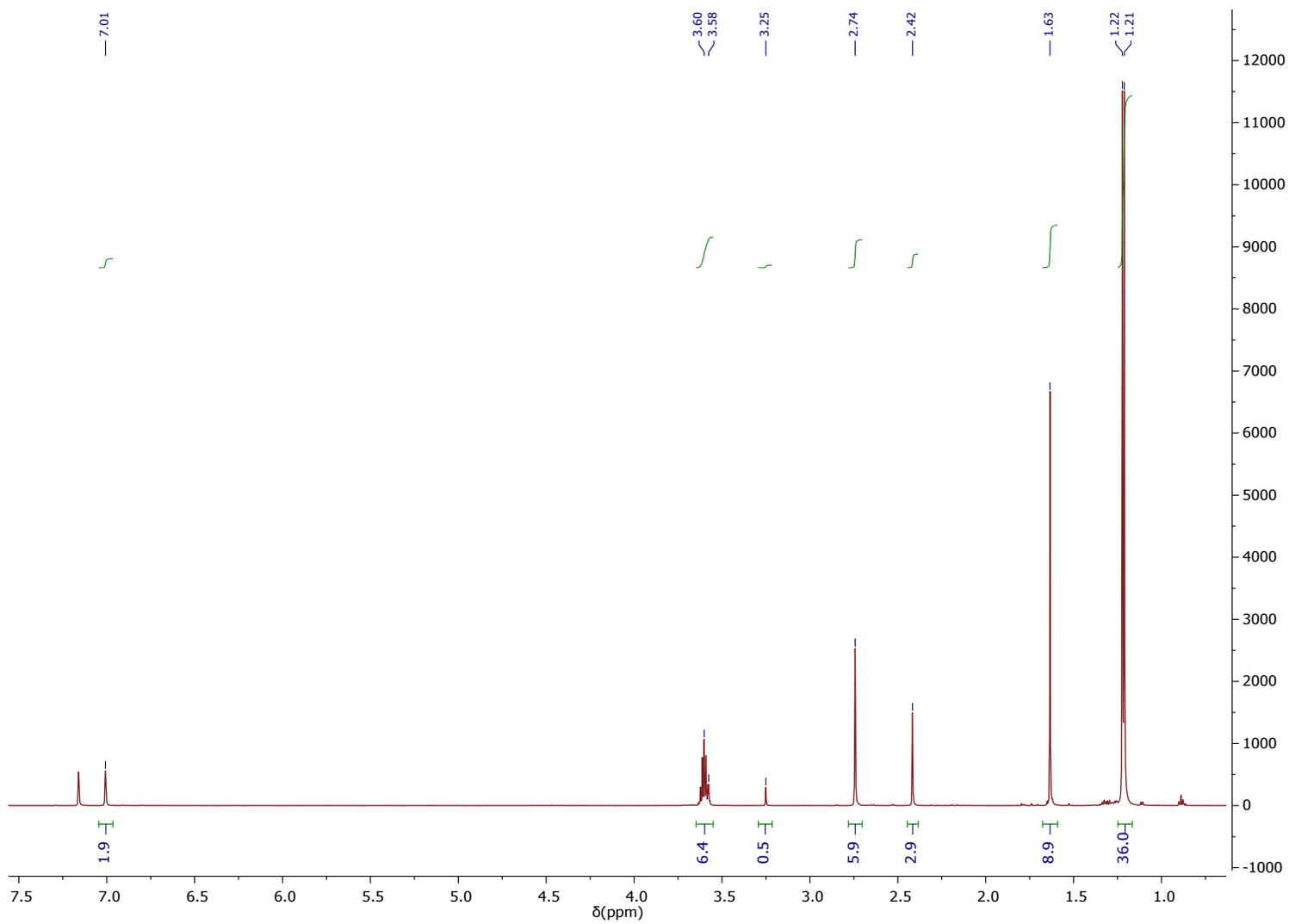


Figure S16. ^1H NMR spectrum of $\text{Th}(\text{PHMe})_3(\text{BIMA})_3$ (**11a**) at 298 K in C_6D_6

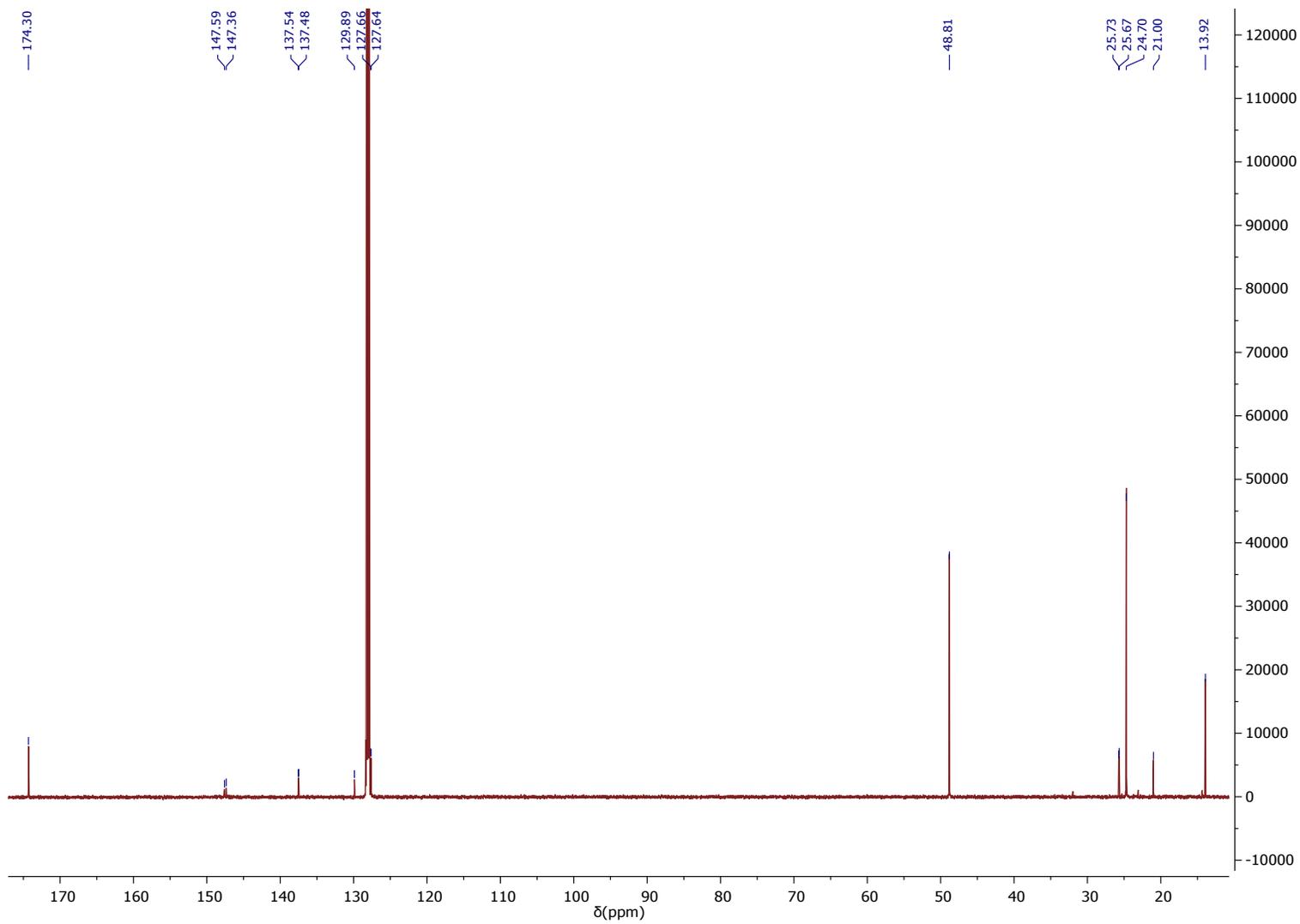


Figure S17. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{Th}(\text{PHMe}_3)(\text{BIMA})_3$ (**11a**) at 298 K in C_6D_6

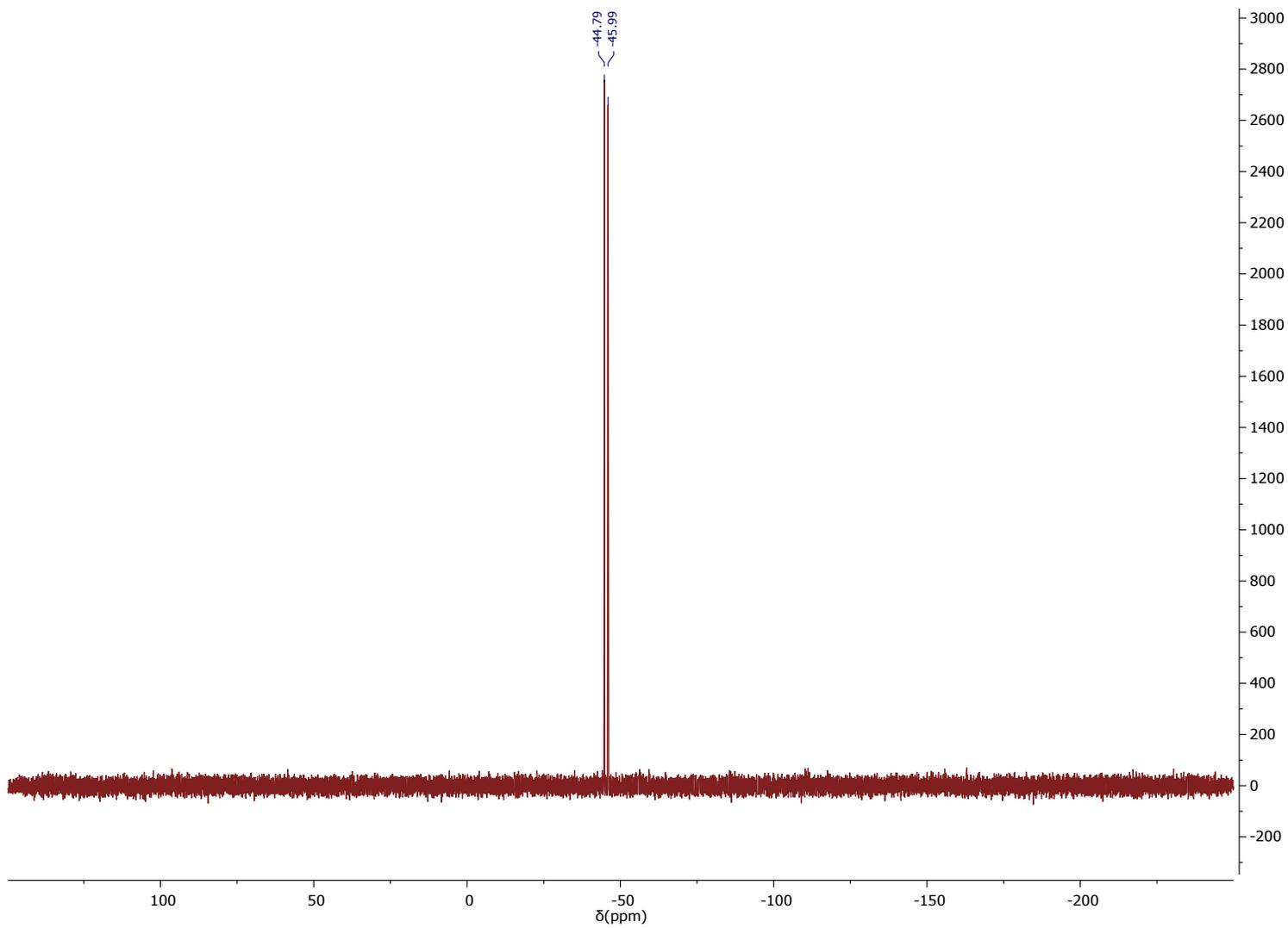


Figure S18. ^{31}P NMR spectrum of $\text{Th}(\text{PHMes})(\text{BIMA})_3$ (**11a**) at 298 K in C_6D_6

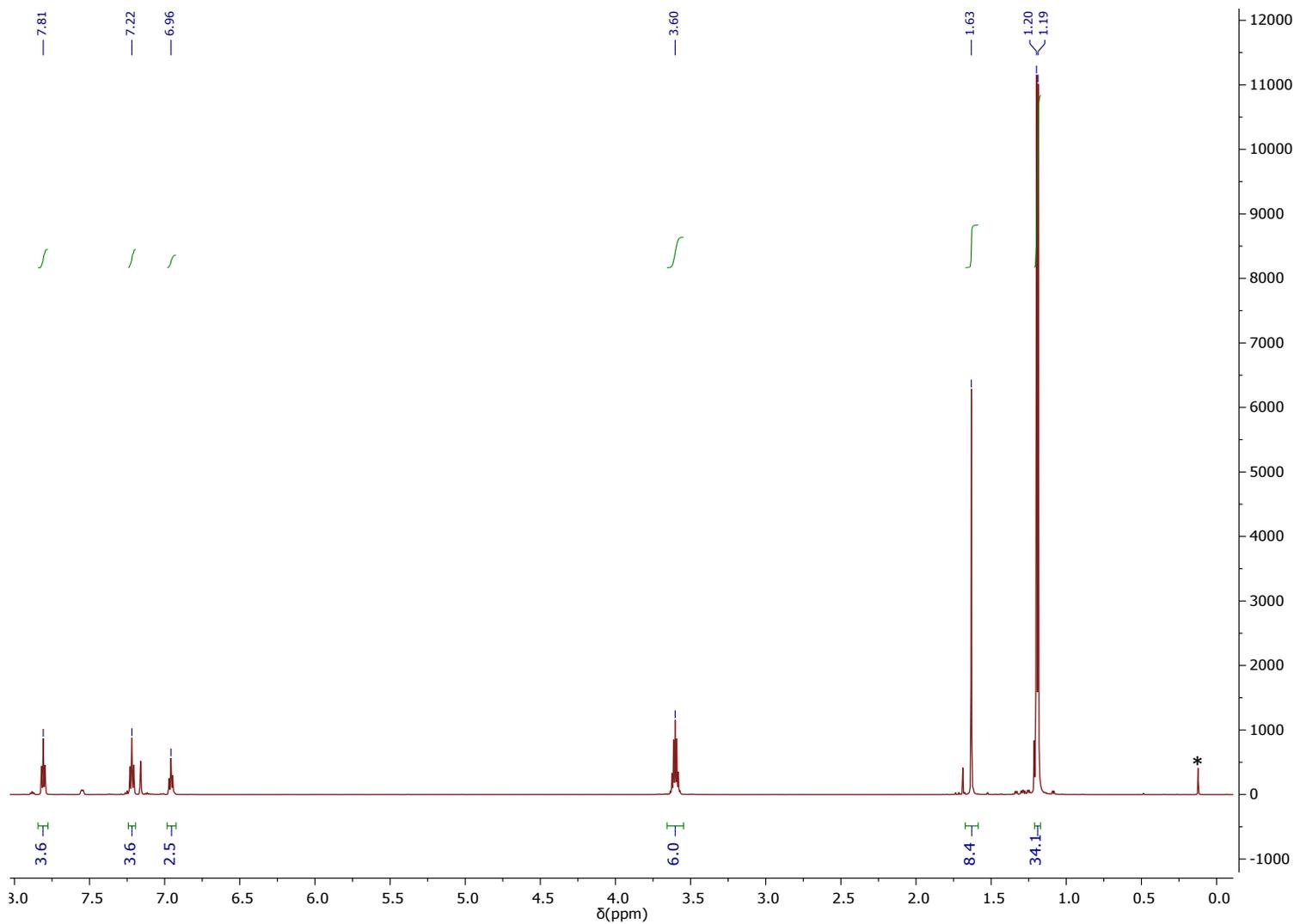


Figure S19. ¹H NMR spectrum of Th(PPh₂)(BIMA)₃ (11b) at 298 K in C₆D₆. *HMDSO

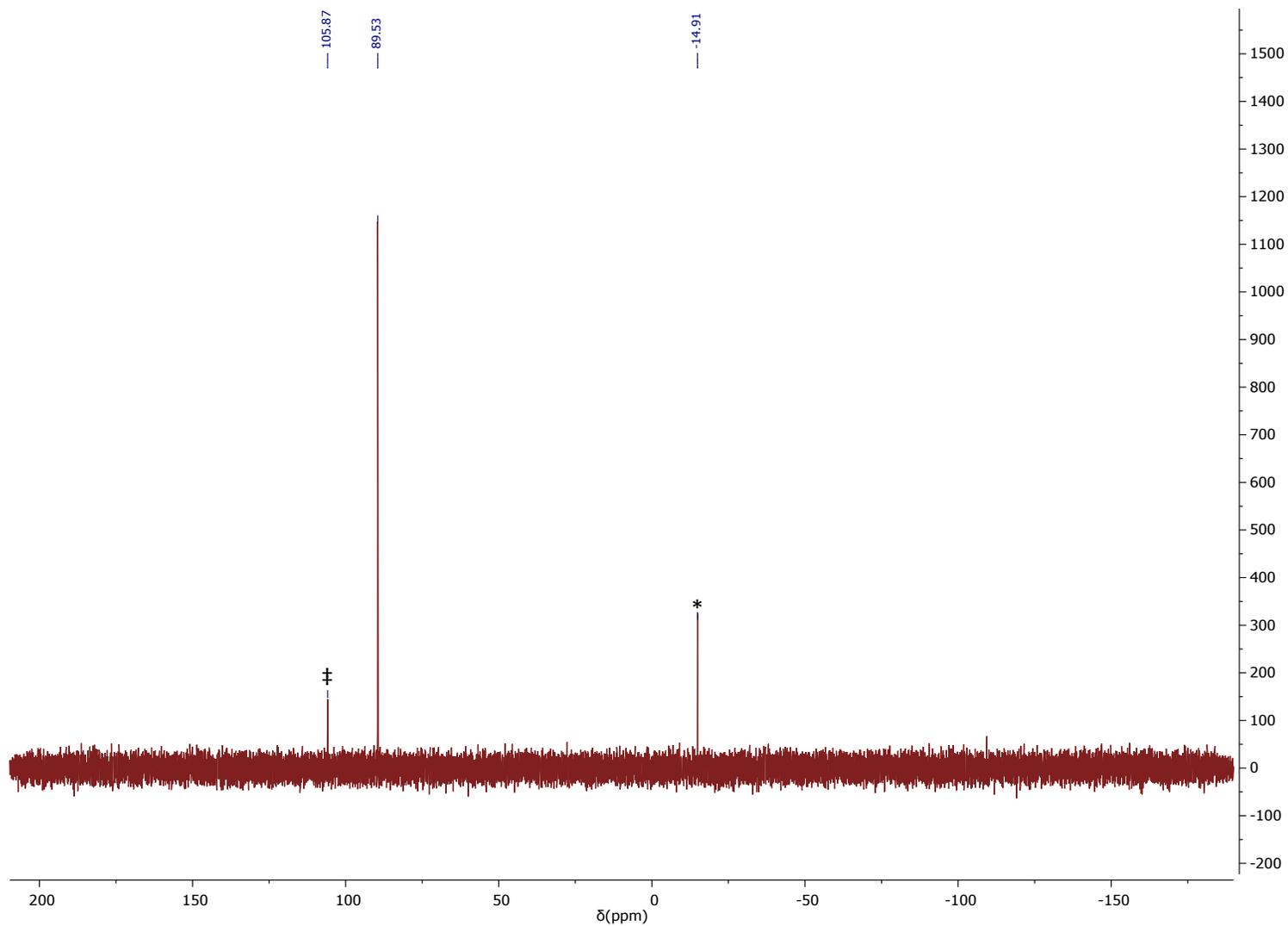


Figure S20. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $\text{Th}(\text{PPh}_2)(\text{BIMA})_3$ (**11b**) at 298 K in C_6D_6 . * $\text{Ph}_2\text{P-PPh}_2$.
‡unidentified phosphorus-containing species

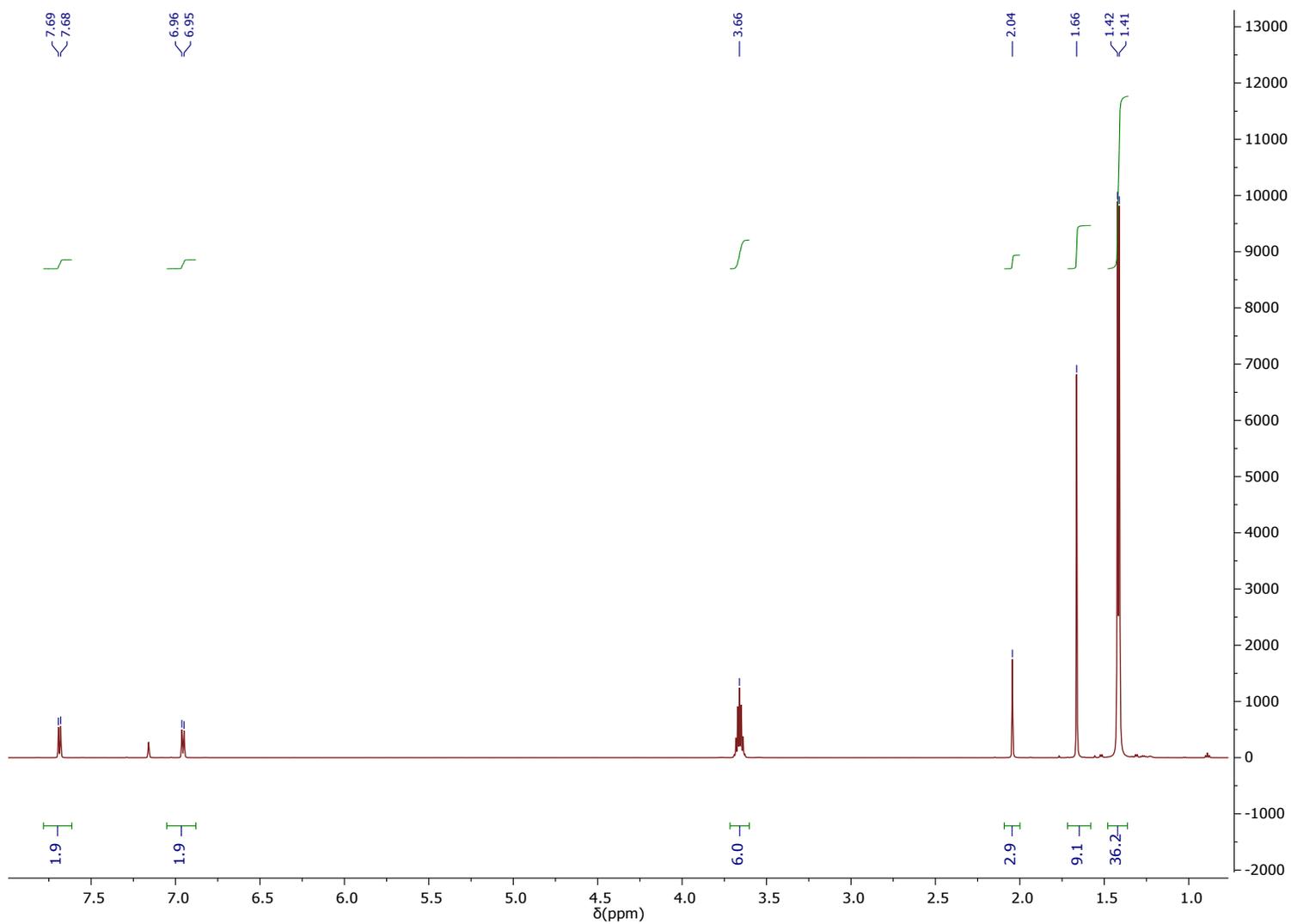


Figure S21. ¹H NMR spectrum of Th(C≡C-*p*-tolyl)(BIMA)₃ (**12**) at 298 K in C₆D₆

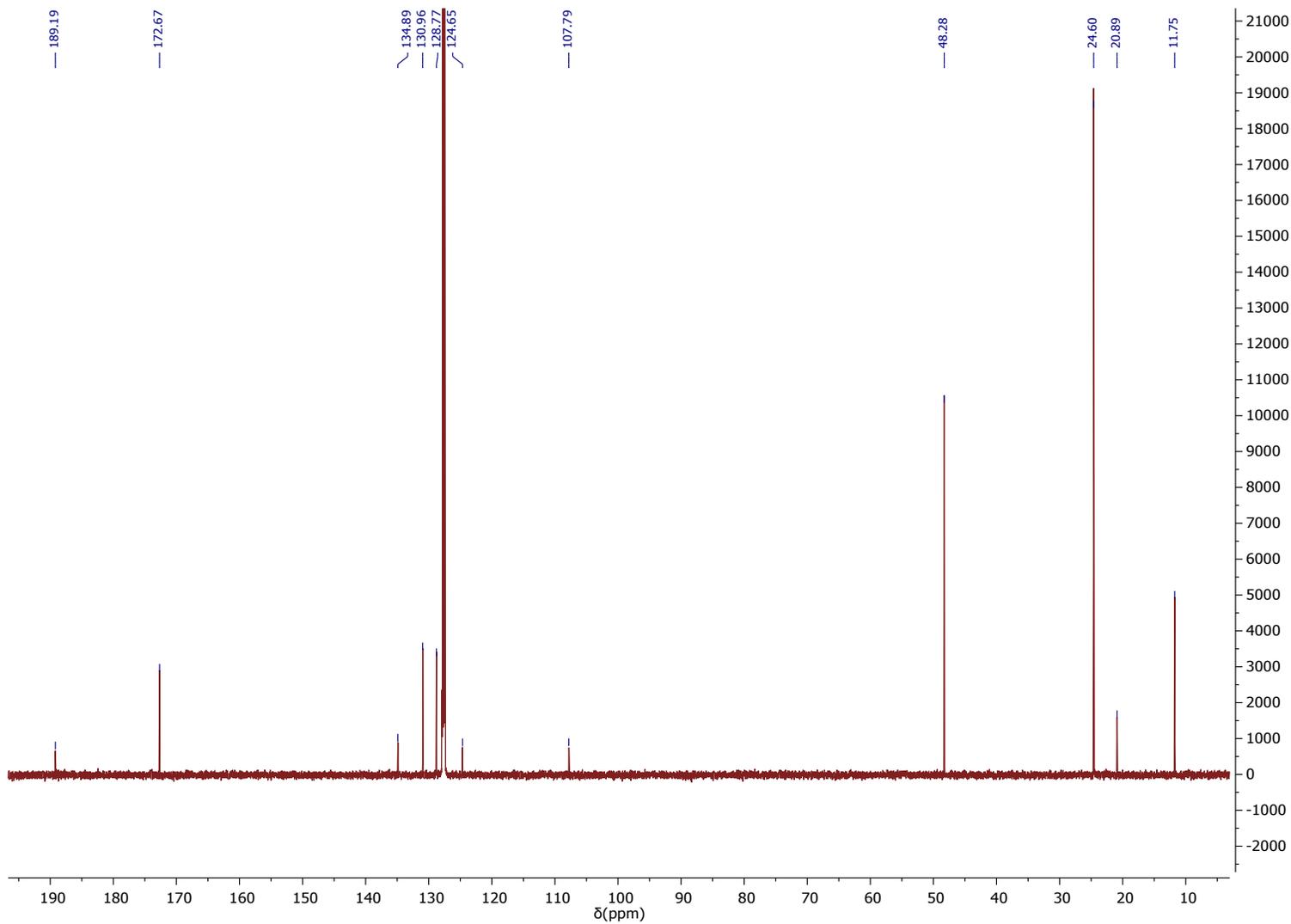


Figure S22. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{Th}(\text{C}\equiv\text{C}-p\text{-tolyl})(\text{BIMA})_3$ (**12**) at 298 K in C_6D_6

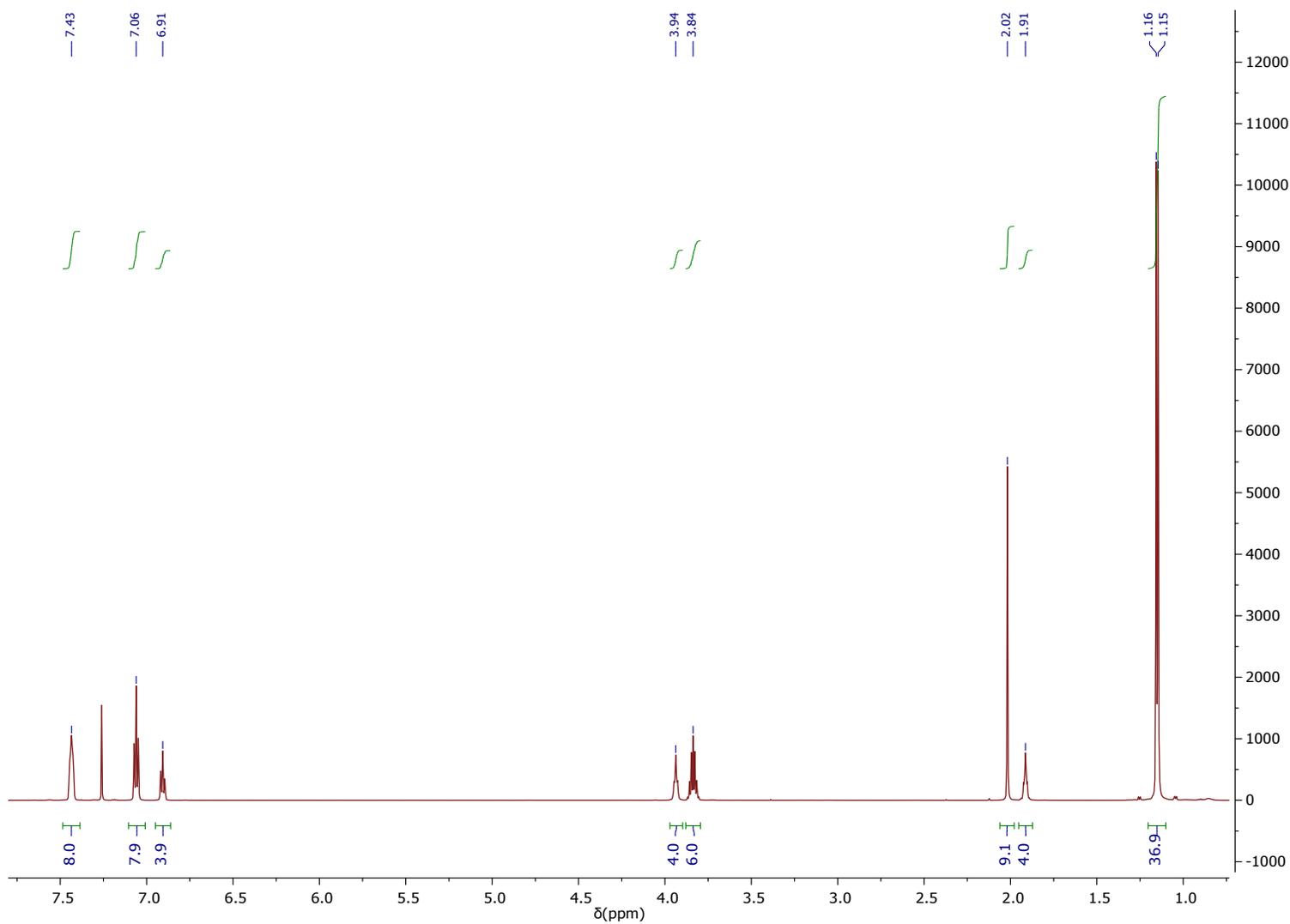


Figure S23. ^1H NMR spectrum of $\text{Th}[(\text{THF})(\text{BIMA})_3][\text{BPh}_4]$ (**13**) at 298 K in CDCl_3

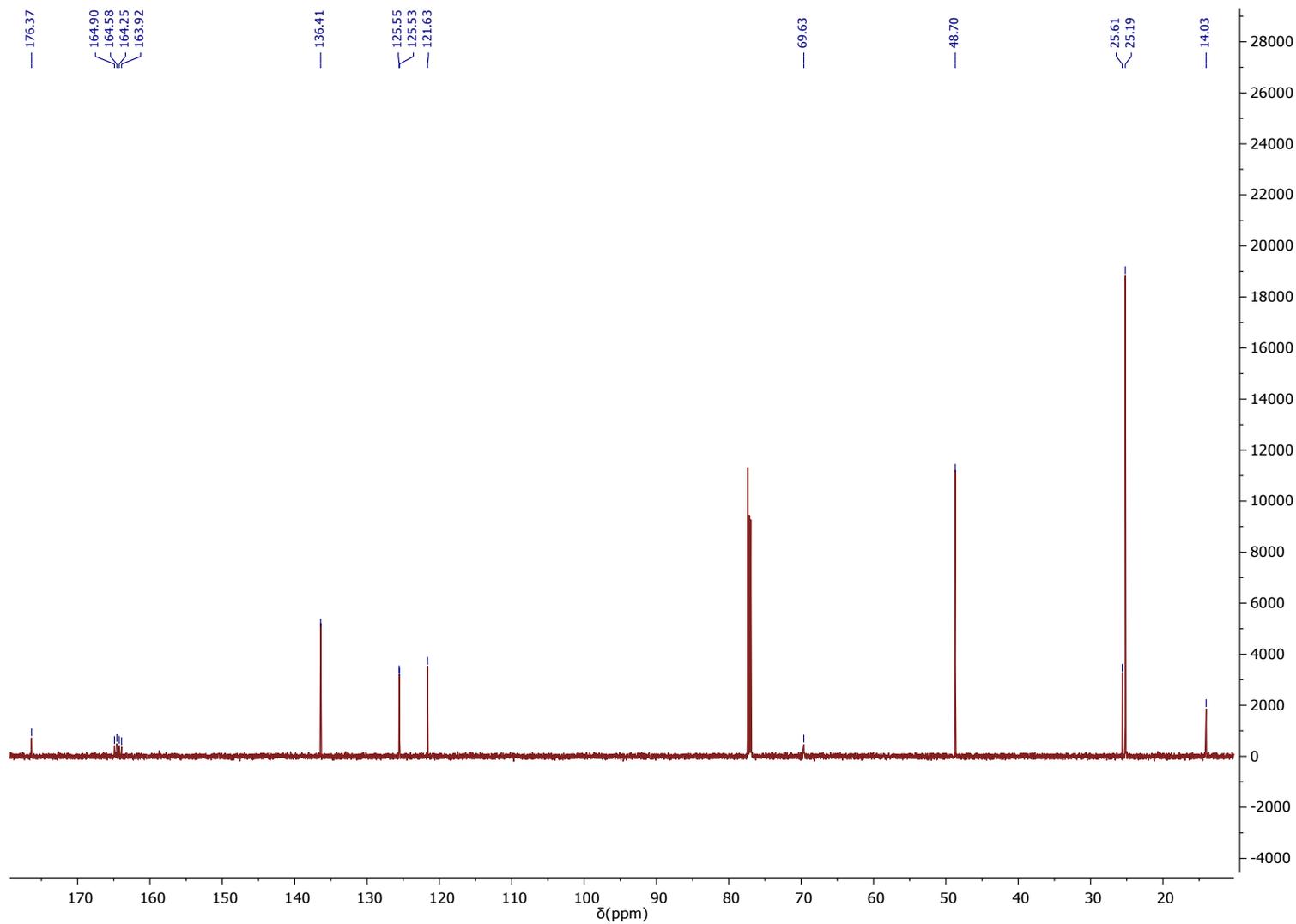


Figure S24. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{Th}[(\text{THF})(\text{BIMA})_3][\text{BPh}_4]$ (**13**) at 298 K in CDCl_3

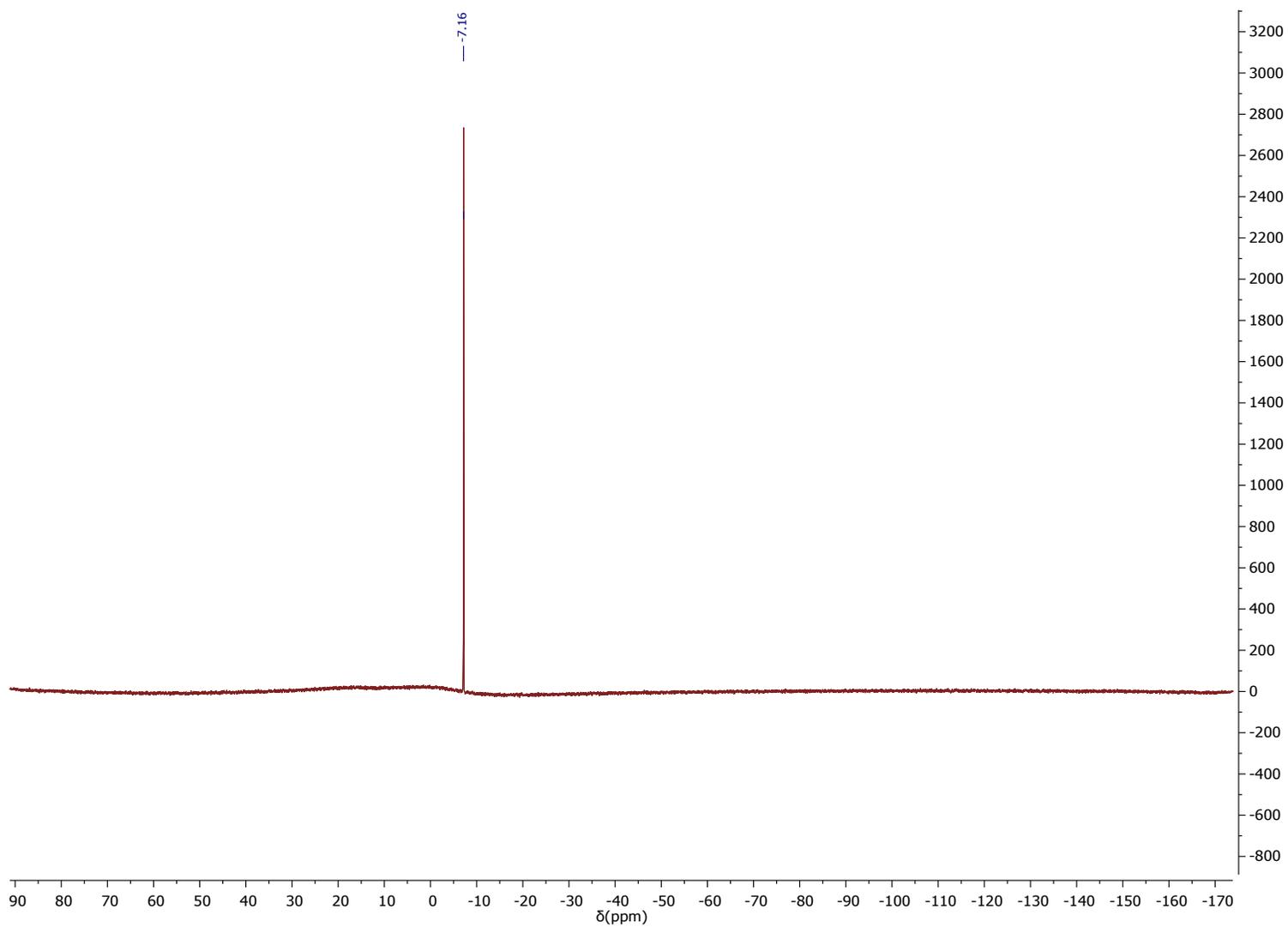


Figure S25. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of $\text{Th}[(\text{THF})(\text{BIMA})_3][\text{BPh}_4]$ (**13**) at 298 K in CDCl_3

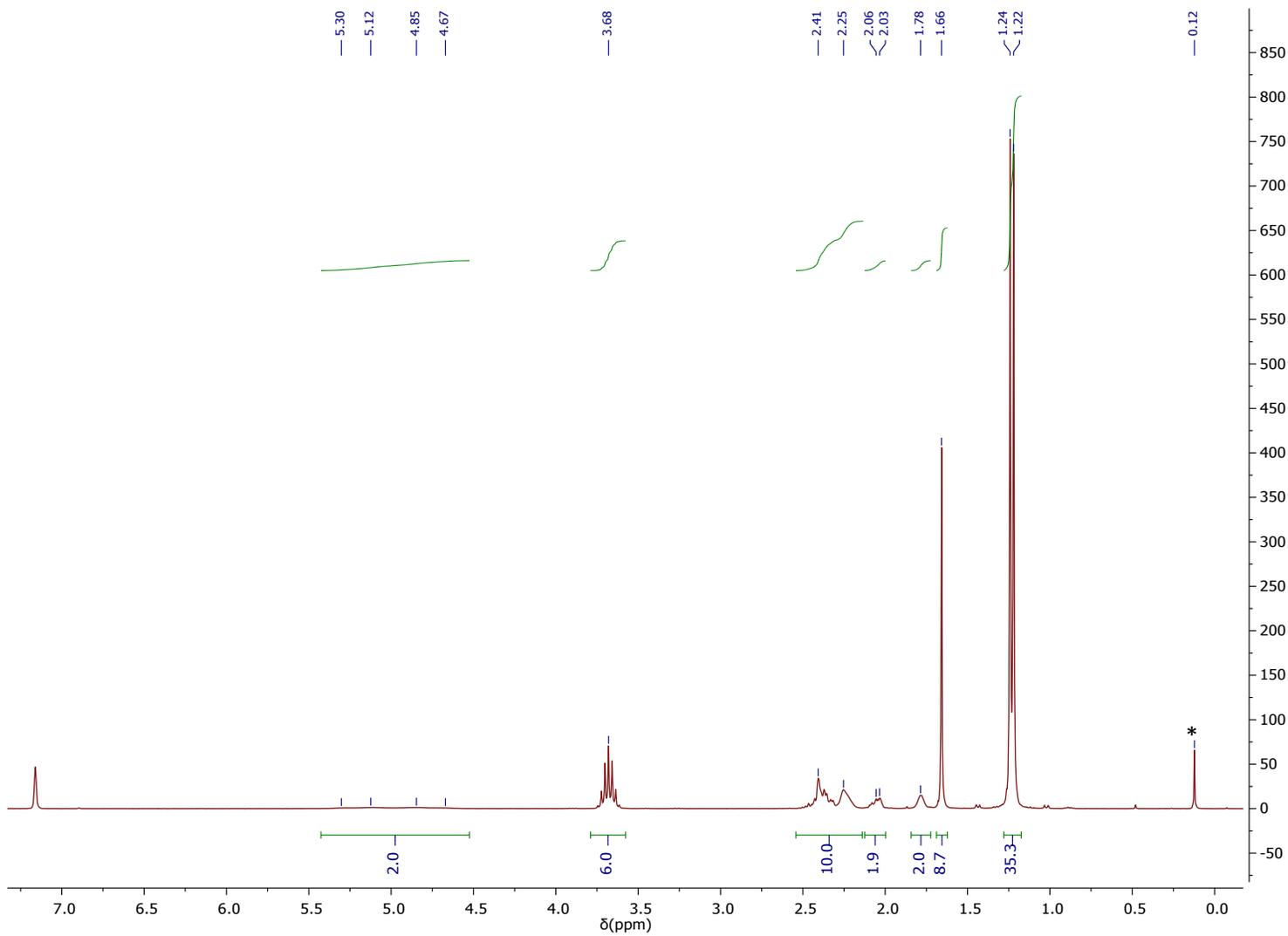


Figure S26. ^1H NMR spectrum of $(\text{BIMA})_3\text{Th}(\mu\text{-H})_2(9\text{-BBN})$ (**14**) at 298 K in C_6D_6 . *HMDSO

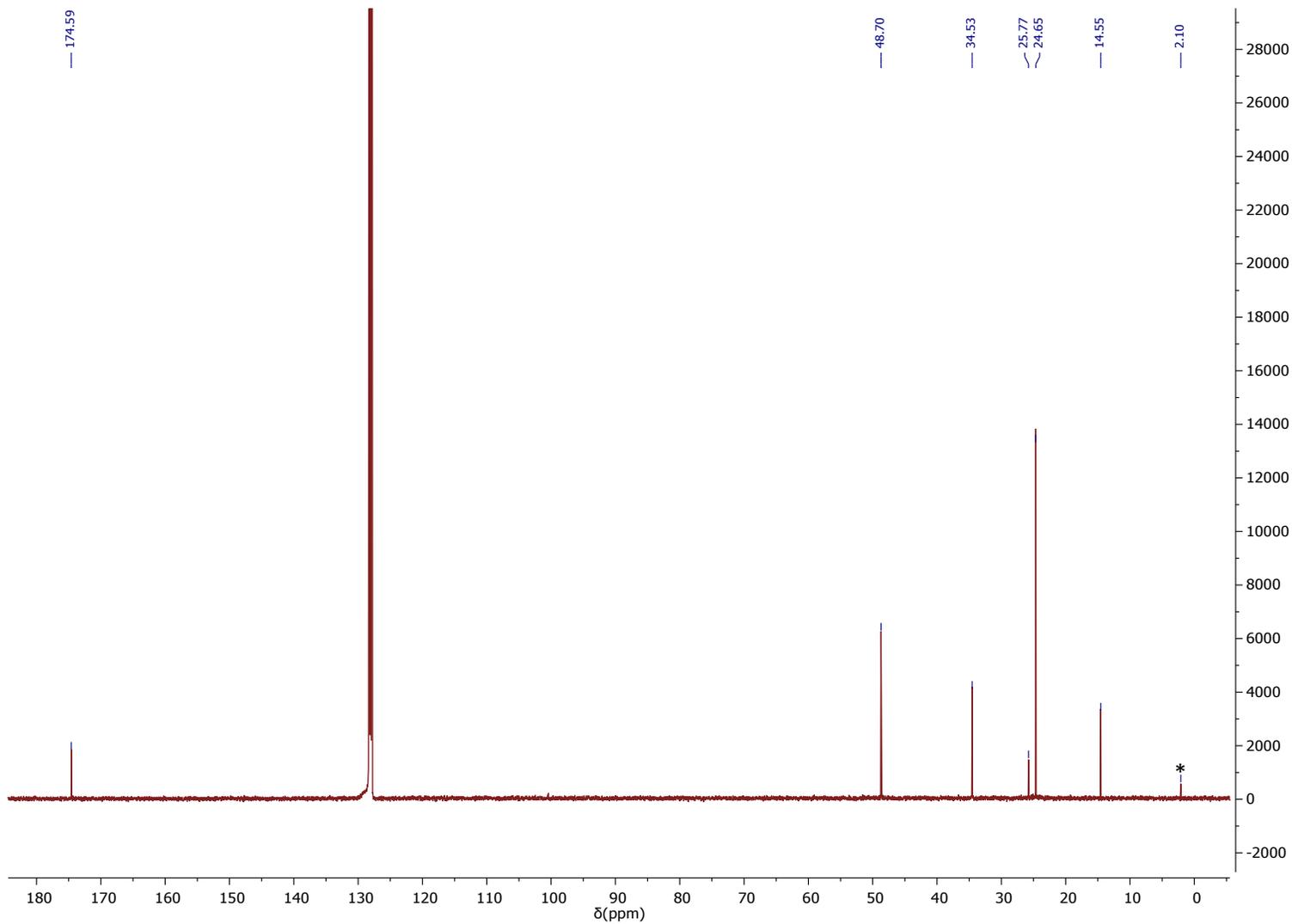


Figure S27. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $(\text{BIMA})_3\text{Th}(\mu\text{-H})_2(9\text{-BBN})$ (**14**) at 298 K in C_6D_6 . *HMDSO

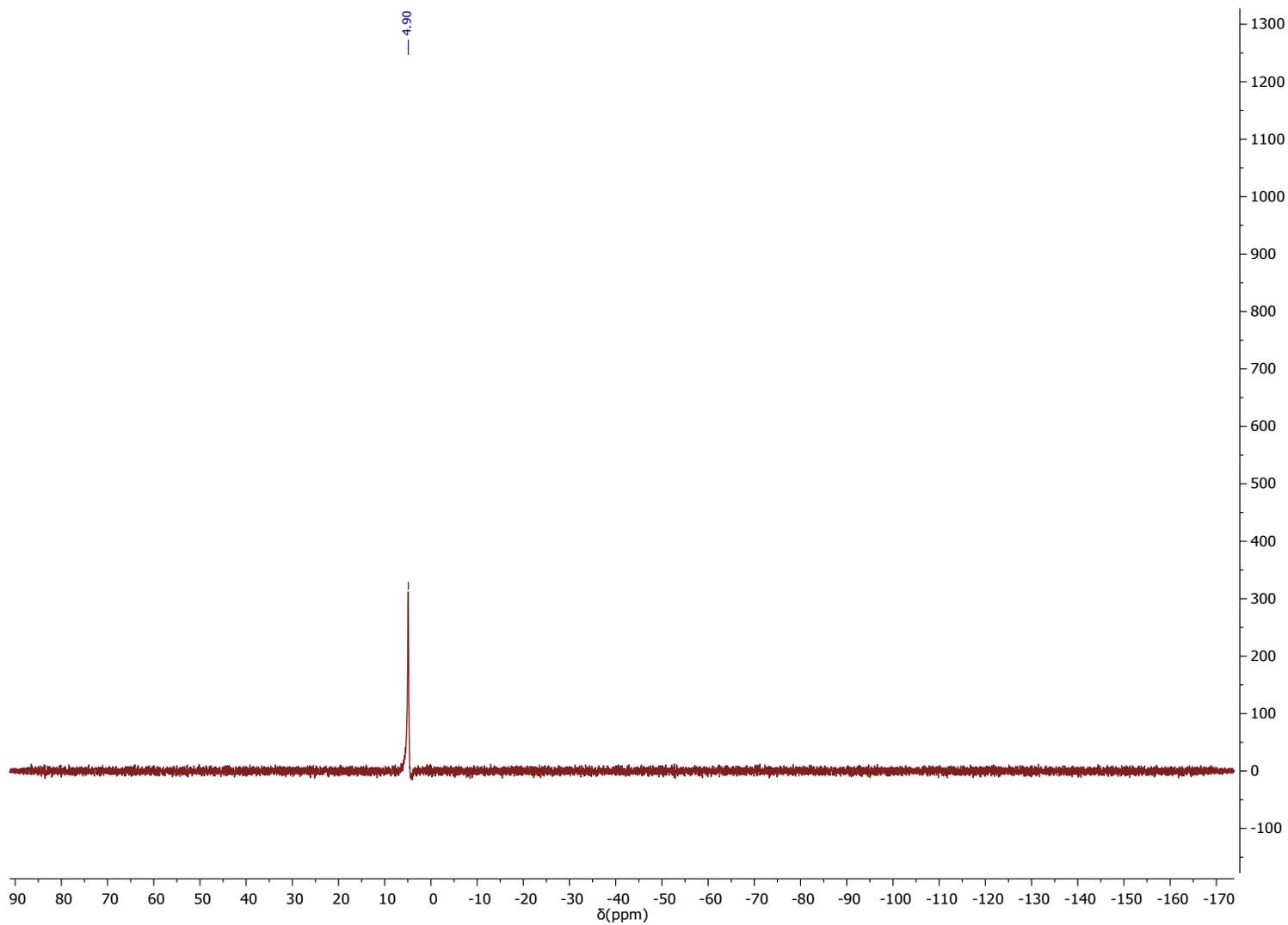


Figure S28. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of $(\text{BIMA})_3\text{Th}(\mu\text{-H})_2(9\text{-BBN})$ (**14**) at 298 K in C_6D_6

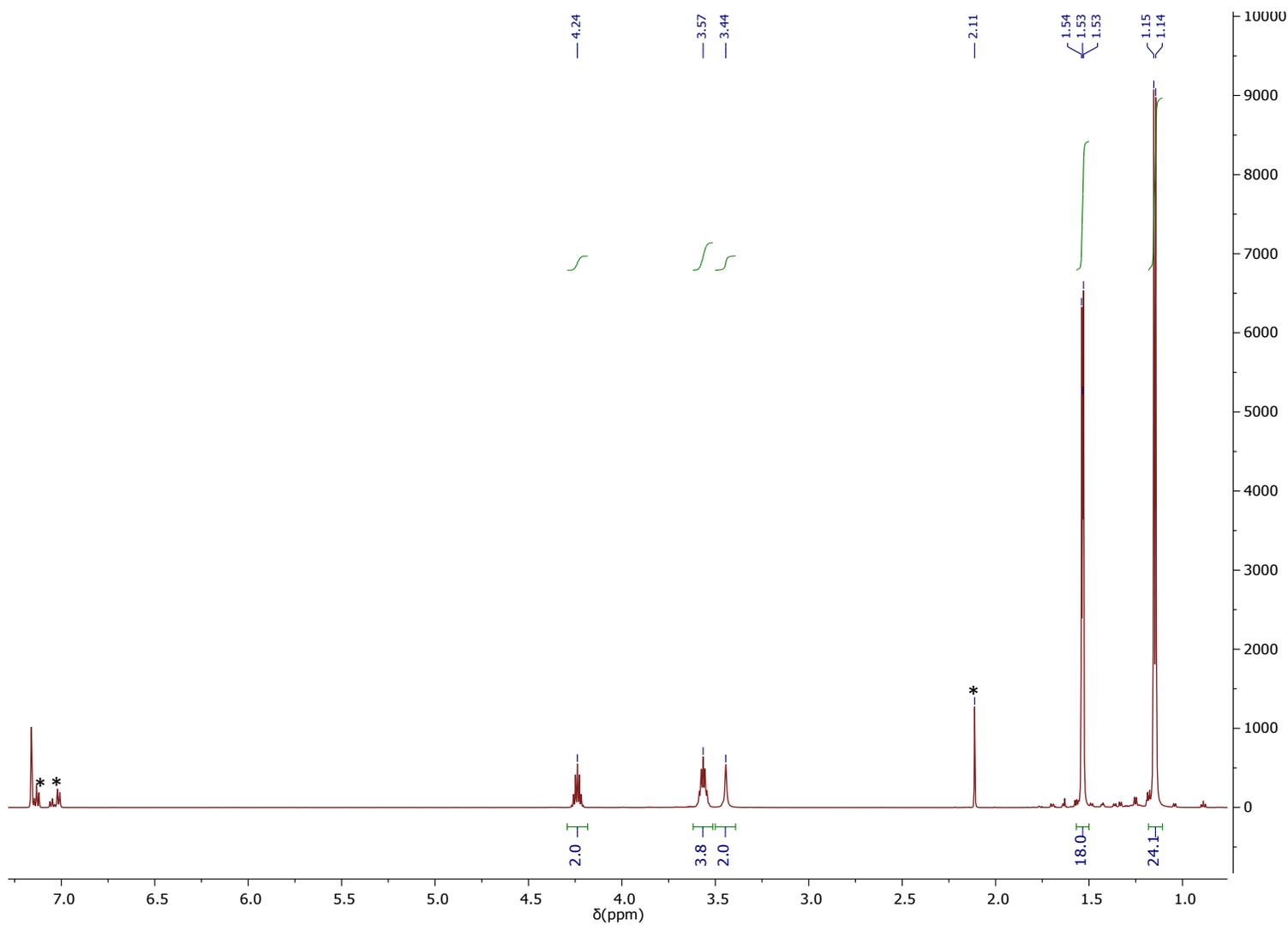


Figure S29. ¹H NMR spectrum of Th(BIMA)₂(BIMA*) (**15**) at 298 K in C₆D₆. *Toluene

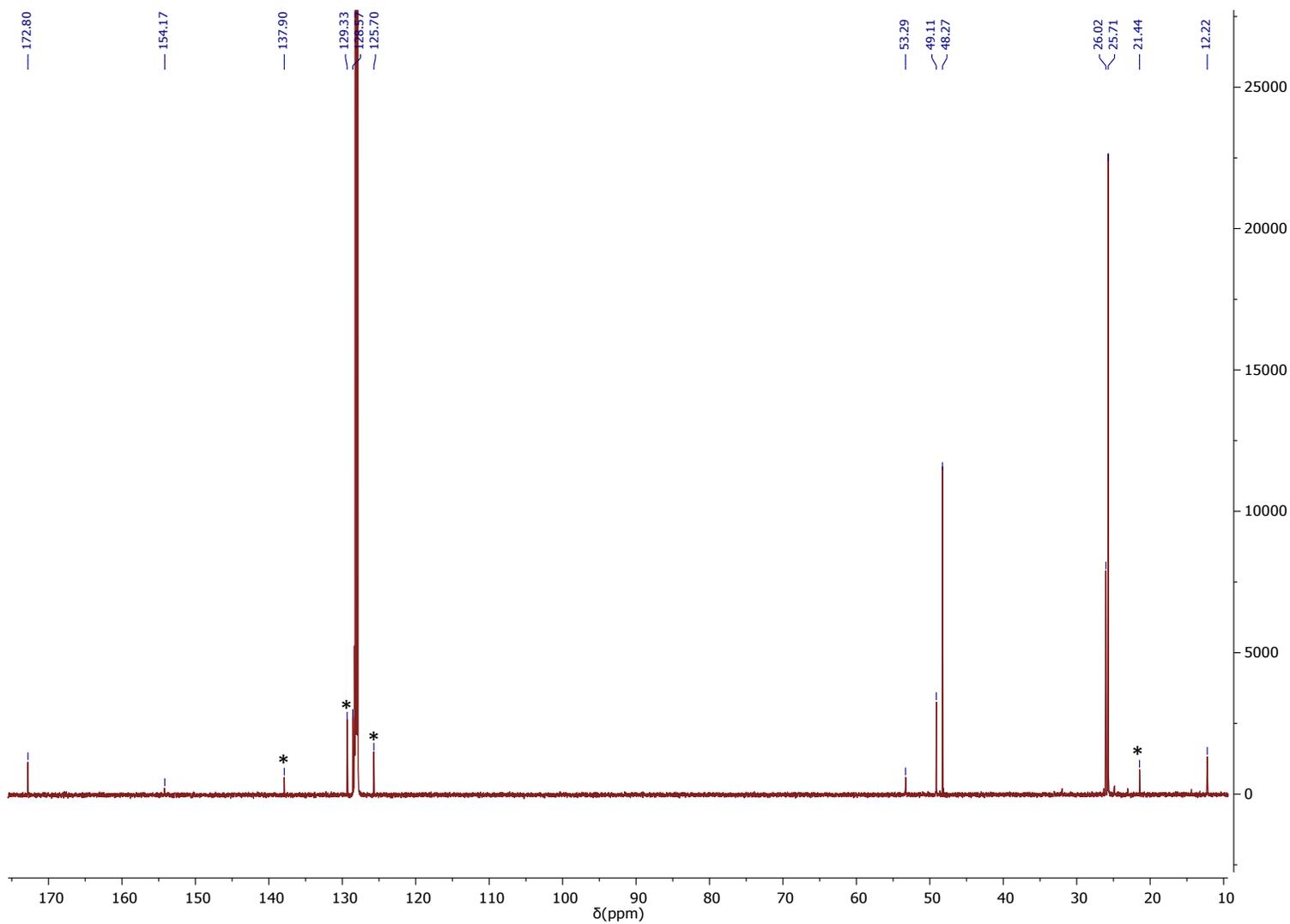


Figure S30. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{Th}(\text{BIMA})_2(\text{BIMA}^*)$ (**15**) at 298 K in C_6D_6 . *Toluene

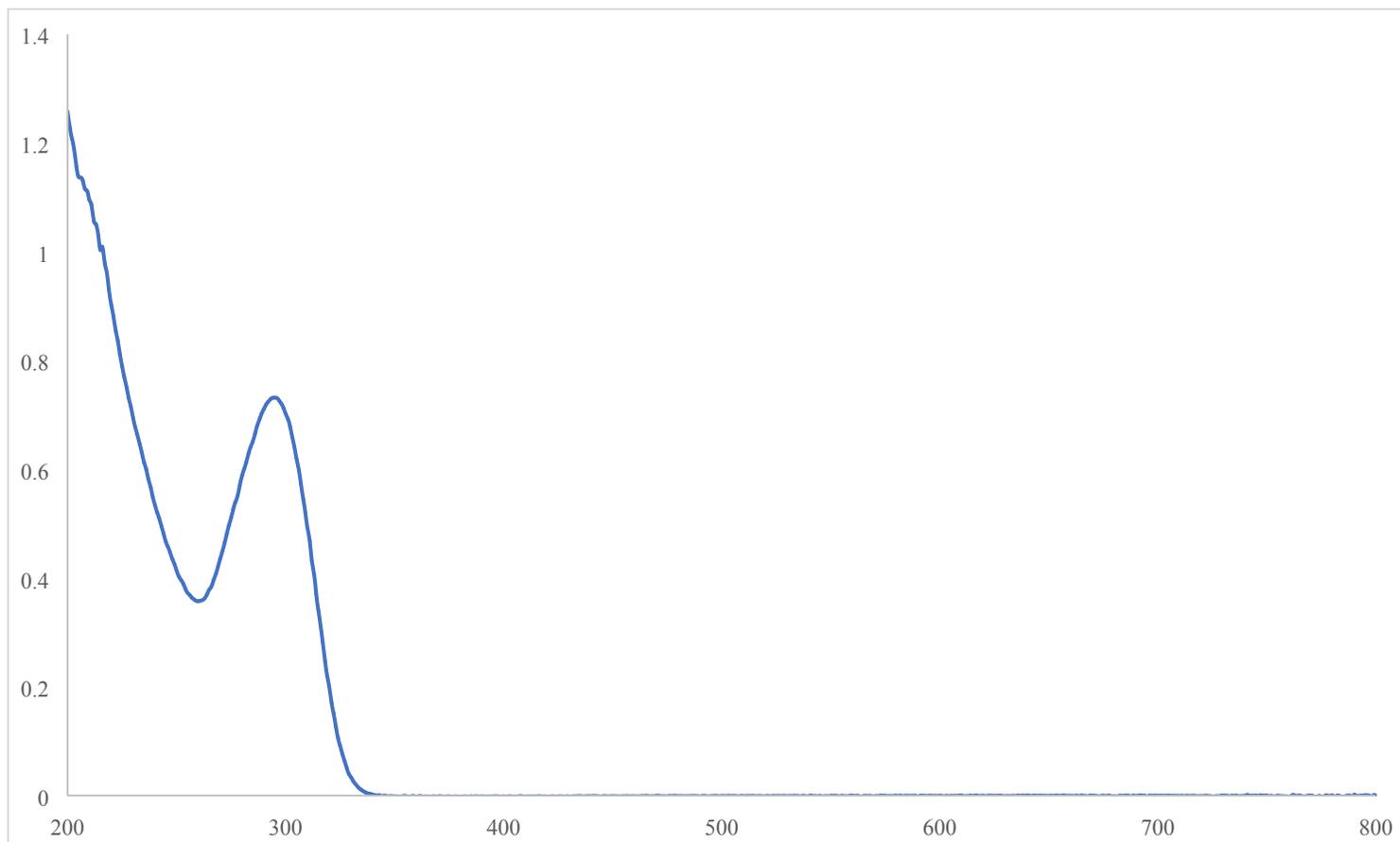


Figure S31. UV-Vis spectrum of $\text{Th}(\text{CH}_2\text{SiMe}_3)(\text{BIMA})_3$ (**1**) in hexane

C. X-ray Crystallography. Single-crystal X-ray diffraction experiments were performed at the UC Berkeley CHEXRAY crystallographic facility. Measurements of all compounds were performed on a Bruker APEX-II area detector using Mo K α radiation ($\lambda = 0.71073$ Å). Crystals were kept at 100(2) K throughout collection. Data collection was performed with Bruker APEX2 software (v. 2014.11). Data refinement and reduction were performed with Bruker SAINT (V8.34A). All structures were solved with SHELXT.53 Structures were refined with SHELXL-2014. Molecular graphics were computed with Mercury 3.10. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were either included at the geometrically calculated positions and refined using a riding model or located as Q peaks in the Fourier difference map.

	2	3	4	5	6	7	11a
Chemical formula	C ₃₂ H ₆₈ N ₈ Th	C ₃₅ H ₆₉ N ₉ SiTh	C ₃₄ H ₆₇ N ₇ SiTh	C ₃₇ H ₇₁ N ₇ SiTh	C ₂₉ H ₆₂ N ₆ OSiTh	C ₃₀ H ₆₂ N ₆ O ₂ SiTh	C ₃₃ H ₆₃ N ₆ PTh
Formula weight	796.99	876.12	834.07	874.15	770.97	798.98	806.92
Colour, habit	Colourless, block	Colourless, block	Colourless, block	Colourless, block	Colourless, block	Colourless, block	Yellow, block
Temperature (K)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	P-1	P 21/c	P 21/n	P 21/n	P-1	P-1	P 21/n
a (Å)	10.3830(4)	16.9023(9)	12.6373(9)	10.9839(5)	12.986(4)	9.4981(19)	22.5782(10)
b (Å)	11.3585(5)	11.4723(6)	17.8743(14)	20.9900(8)	16.992(5)	11.950(2)	13.2908(6)
c (Å)	17.4827(8)	21.7432(12)	17.1544(13)	18.2460(8)	17.337(4)	16.888(3)	25.4828(11)
α (°)	89.7768(18)	90	90	90	103.843(10)	90.32(3)	90
β (°)	89.4038(16)	95.127(3)	90.033(3)	93.4600(18)	97.592(10)	99.06(3)	100.332(2)
γ (°)	63.7604(15)	90	90	90	93.871(12)	102.29(3)	90
V (Å ³)	1849.26(14)	4199.3(4)	3874.9(5)	4199.0(3)	3662.2(17)	1848.0(7)	7522.9(6)
Z	2	4	4	4	2	2	4
Density (Mg m ⁻³)	1.431	1.386	1.430	1.383	1.398	1.436	1.425
F(000)	812	1784	1696	1784	1560	808	3264
Radiation Type	MoK _α	MoK _α	MoK _α	MoK _α	MoK _α	MoK _α	MoK _α
μ (mm ⁻¹)	4.063	3.613	3.910	3.612	4.132	4.099	3.613
Crystal size (mm ³)	0.18 x 0.20 x 0.20	0.05 x 0.05 x 0.10	0.10 x 0.22 x 0.25	0.15 x 0.20 x 0.20	0.15 x 0.24 x 0.29	0.05 x 0.10 x 0.13	0.15 x 0.22 x 0.40
Meas. Refl.	53843	142853	176871	60423	118651	148820	169945
Indep. Refl.	6800	15081	7927	7751	15074	5516	18721
R(int)	0.0291	0.0441	0.0315	0.0279	0.0399	0.0422	0.0414
Final R indices [I > 2σ(I)]	R = 0.0107 R _w = 0.0273	R = 0.0317 R _w = 0.0700	R = 0.0153 R _w = 0.0309	R = 0.0220 R _w = 0.0470	R = 0.0273 R _w = 0.0556	R = 0.0198 R _w = 0.0453	R = 0.0252 R _w = 0.0510
Goodness-of-fit	1.090	1.089	1.062	1.072	1.109	1.099	1.042
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.499, -0.498	1.383, -1.210	1.145, -0.484	1.103, -1.137	3.302, -2.439	2.310, -0.709	1.986, -1.880
CCDC	1811106	1811107	1811108	1811109	1811110	1811111	1811112

	12	13	14	15
Chemical formula	C ₃₃ H ₅₈ N ₆ Th	C ₅₆ H ₈₇ N ₆ O ₂ BTh	C ₃₂ H ₆₇ BN ₆ Th	C ₂₄ H ₅₀ N ₆ Th
Formula weight	770.91	1119.16	778.76	654.74
Colour, habit	Colourless, block	Colourless, rod	Colourless, block	Colourless, block
Temperature (K)	100(2)	100(2)	100(2)	100(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	P 21/c	P 21/c	P 21/n	P-1
a (Å)	19.0249(9)	18.6971(7)	12.1573(13)	11.5082(5)
b (Å)	10.3942(5)	15.8036(5)	18.4711(18)	12.3194(5)
c (Å)	19.1330(9)	18.9111(6)	16.3766(18)	12.8462(5)
α (°)	90	90	90	61.8432(7)
β (°)	110.1048(18)	103.688(2)	90.215(5)	79.1570(8)
γ (°)	90	90	90	86.2752(8)
V (Å ³)	3553.0(3)	5429.2(3)	3677.5(7)	1576.47(11)
Z	4	4	4	4
Density (Mg m ⁻³)	1.441	1.369	1.407	1.468
F(000)	1552	2304	1584	694
Radiation Type	MoK _α	MoK _α	MoK _α	MoK _α
μ (mm ⁻¹)	4.226	4.129	4.083	4.753
Crystal size (mm ³)	0.08 x 0.08 x 0.12	0.02 x 0.02 x 0.05	0.05 x 0.05 x 0.05	0.10 x 0.10 x 0.10
Meas. Refl.	81894	138819	193336	47536
Indep. Refl.	6536	10015	6764	5773
R(int)	0.0265	0.0508	0.0484	0.0263
Final R indices [I > 2σ(I)]	R = 0.0148 R _w = 0.0320	R = 0.0204 R _w = 0.0407	R = 0.0207 R _w = 0.0452	R = 0.0207 R _w = 0.0488
Goodness-of-fit	1.102	1.068	1.103	1.117
Δρ _{max} , Δρ _{min} (e Å ⁻³)	1.363, -0.615	1.452, -0.967	1.291, -0.758	2.661, -1.099
CCDC	1811113	1811114	1811115	1811116

D. References

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