

Electronic Supporting Information

Alkene Isomerization by “Sandwich” Diimine-Palladium Catalysts

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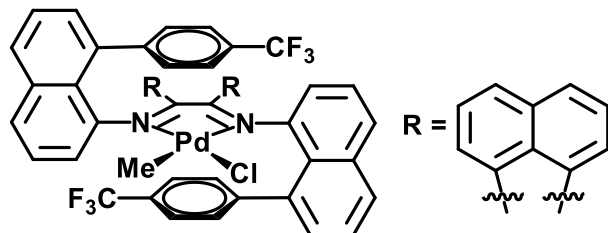
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General Considerations

Reactions were performed using standard glassware or were run in 2-dram vials with PTFE/Liner screw caps. Column chromatography was performed on 60Å silica gel (Silicycle). The ^1H , ^{13}C , ^{19}F and 2D-NMR spectra were recorded on JEOL EC-400, JEOL EC-500, or JEOL EC-600 spectrometers using the residual solvent peak as a reference. Analytical thin layer chromatography was performed on silica gel TLC Al foils with a fluorescent indicator (254 nm) from Fluka. Low temperature reactions were performed using a Cryo Immersion Cooler FC100 with Flexi Probe from SP Scientific. Elemental analyses were performed by Atlantic Microlabs Inc. (Norcross, GA, USA). All procedures were performed under ambient air unless otherwise noted. Reagents and starting materials were obtained from commercial sources and used without further purification unless otherwise noted. Ligand,¹ (COD)PdMeCl,² NaBArF (sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate),³ and silyl allyl ethers⁴ were made according to the known procedures. Hexene was distilled from sodium under nitrogen and methylene chloride was purified on a Pure Process Technology solvent purification system.

Synthesis of Catalyst



Catalyst **12** was synthesized using a modified literature procedure.⁵ To a flame dried 50 mL Schlenk flask, ligand (1.00 g, 1.39 mmol) was added under a positive pressure of nitrogen and sealed with a rubber septum. The flask was

evacuated and backfilled with nitrogen three times and transferred into a glovebox. In a nitrogen filled glovebox (COD)PdMeCl (367 mg, 1.39 mmol) was added and the flask was sealed with a rubber septum. Outside the glovebox CH₂Cl₂ (28 mL) was added and the flask was covered with aluminum foil. The resulting solution was stirred for 40 hours at room temperature. The mixture was concentrated on silica and purified by column chromatography on silica gel (eluent hexanes:EtOAc 5/1 to 2/1) to afford 763 mg of **12** (63%) as a red solid. $R_f = 0.69$ (1:1 Hexanes/Ethyl Acetate)

¹H NMR (500 MHz, CDCl₃, ppm) δ 8.12 – 7.89 (m, 10H), 7.77 (t, ³ $J_{HH} = 7.7$ Hz, 1H), 7.71 (t, ³ $J_{HH} = 7.7$ Hz, 1H), 7.59 – 7.43 (m, 2H), 7.33 (d, ³ $J_{HH} = 7.2$ Hz, 1H), 7.22 (t, ³ $J_{HH} = 7.7$ Hz, 1H), 7.16 (t, ³ $J_{HH} = 7.7$ Hz, 1H), 7.10 (d, ³ $J_{HH} = 6.9$ Hz, 1H), 7.06 (d, ³ $J_{HH} = 7.2$ Hz, 1H), 7.03 (d, ³ $J_{HH} = 6.9$ Hz, 1H), 6.67 (d, ³ $J_{HH} = 7.8$ Hz, 1H), 6.28 (d, ³ $J_{HH} = 7.3$ Hz, 1H), 6.16 (d, ³ $J_{HH} = 7.8$ Hz, 1H), 6.10 (d, ³ $J_{HH} = 7.7$ Hz, 1H), 6.00 (d, ³ $J_{HH} = 7.8$ Hz, 1H), 5.91 (d, ³ $J_{HH} = 7.3$ Hz, 1H), 0.48 (s, 3H).

¹³C NMR (126 MHz, CDCl₃, ppm) δ 170.5, 165.4, 146.5, 146.3, 143.2, 142.3, 141.1, 136.5, 135.2, 134.8, 133.2, 131.7, 131.2, 131.0, 130.7, 130.4, 129.7, 129.6, 129.1, 128.4, 128.3, 127.1, 126.8, 125.9, 125.8, 125.7, 125.6, 125.3, 124.4, 124.1, 123.9, 122.9, 122.9, 122.6, 121.5, 1.1.

¹⁹F NMR (470 MHz, CDCl₃, ppm) δ -61.9, -62.1.

Anal. Calcd. for C₄₇H₂₉ClF₆N₂Pd: C 64.32; H 3.33; N 3.19; found C 62.23; H 3.13; N 3.58.

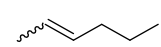
Isomerization of 1-Olefins to 2-Olefins

General Procedure for Isomerization of 1-Olefins to 2-Olefins

A 2-dram vial with a screw cap (PTFE/Liner) equipped with a magnetic stir bar was charged with NaBARf (7 mg, 8 μ mol) and olefin (0.2 mmol). Freshly prepared solutions of catalyst **12** (5 mM in CDCl₃) and PhSiH₃ (60 mM in CDCl₃) were cooled to 0 °C. The precooled catalyst solution

(0.4 mL, 2 μ mol) was added to the vial followed by the addition of the precooled silane solution (0.1 mL of a 60 mM solution in CDCl_3 , 6 μ mol) at 0 $^\circ\text{C}$. Sequence of addition is crucial for obtaining high yields. The vial was sealed, placed in a cooling bath at 0 $^\circ\text{C}$ and allowed to stir for the specified time. After the reaction had finished, tert-butyl isocyanide (approximately 6 μ L, >20 equiv. to catalyst) was added and the mixture was shaken to quench the reaction. The solution immediately turned from deep red to orange. An internal standard (1,4-bis(trifluoromethyl)benzene (7.8 μ L, 0.050 mmol) or pyridine (8.1 μ L, 0.010 mmol)) was added to the vial and the whole reaction mixture was transferred to an NMR tube. Either the allylic – CH_3 , allylic – CH_2 , or olefin signal was used for quantification based on the best resolution in the spectra. Spectra were taken with a delay time of 20 seconds. The signal used for quantification is designated in bold in each entry. The signal for tert-butyl isocyanide used to quench the reaction appears at 1.42 ppm.

2-Hexene (Table 1, Entry 1)

 1-Hexene (25 μ L, 0.20 mmol) and NaBARF (7.0 mg, 8.0 μ mol) were added to a 2-dram vial with a screw cap (PTFE/Liner) equipped with a magnetic stir bar. Freshly prepared solutions of catalyst **12** (5 mM in CDCl_3) and PhSiH_3 (60 mM in CDCl_3) were cooled to 0 $^\circ\text{C}$. The precooled catalyst solution (0.4 mL, 2 μ mol) was added to the vial followed by the addition of the precooled silane solution (0.1 mL of a 60 mM solution in CDCl_3 , 6 μ mol) at 0 $^\circ\text{C}$ and stirred for 45 min. After the reaction had finished, tert-butyl isocyanide (approximately 6 μ L, >20 equiv. to catalyst) was added and the mixture was shaken to quench the reaction. 1,4-Bis(trifluoromethyl)benzene (7.8 μ L, 0.050 mmol) was used as an internal standard. ^1H NMR analysis revealed 80% of 2-hexene ($E:Z = 2.1/1$), 7% of 3-hexenes, and 1.5% of 1-hexene. This product is known.¹²

^1H NMR (500 MHz, CDCl_3 , ppm) δ 5.56 – 5.30 (m, 1H, E and Z signals overlap), 2.07 – 1.88 (m, 2H, E and Z signals overlap), **1.64 (Z, dd, $^3J_{\text{HH}} = 3.3$ Hz, $^4J_{\text{HH}} = 1.1$ Hz, 3H)**, **1.60 (E, d, $^3J_{\text{HH}} = 6.2$ Hz, 3H)**, 1.38 – 1.32 (m, 3H, E and Z signals partially overlap with tBuNC), 0.85-0.92 (m, 3H, E and Z signals overlap).

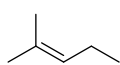
1-Methylcyclohexene (Table 1, Entry 2)



Methylenecyclohexane (24 μL , 0.20 mmol) and NaBARF (7.0 mg, 8.0 μmol) were added to a 2-dram vial with a screw cap (PTFE/Liner) equipped with a magnetic stir bar. Freshly prepared solutions of catalyst **12** (5 mM in CDCl_3) and PhSiH_3 (60 mM in CDCl_3) were cooled to 0 $^\circ\text{C}$. The precooled catalyst solution (0.4 mL, 2 μmol) was added to the vial followed by the addition of the precooled silane solution (0.1 mL of a 60 mM solution in CDCl_3 , 6 μmol) at 0 $^\circ\text{C}$ and stirred for 6 hrs. After the reaction had finished, tert-butyl isocyanide (approximately 6 μL , >20 equiv. to catalyst) was added and the mixture was shaken to quench the reaction. 1,4-Bis(trifluoromethyl)benzene (7.8 μL , 0.050 mmol) was used as an internal standard. ^1H NMR analysis revealed 94% of 1-methylcyclohexene. This product is known.⁶

^1H -NMR (500 MHz, CDCl_3 , ppm) δ **5.33-5.41 (m, 1H)**, 1.92-1.98 (m, 2H), 1.87-1.92 (m, 2H), 1.68 – 1.57 (m, 5H), 1.49-1.57 (m, 2H).

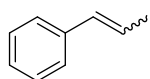
2-Methyl-2-pentene (Table 1, Entry 3)



2-Methyl-1-pentene (24.8 μL , 0.200 mmol) and NaBARF (7.0 mg, 8.0 μmol) were added to a 2-dram vial with a screw cap (PTFE/Liner) equipped with a magnetic stir bar. Freshly prepared solutions of catalyst **12** (5 mM in CDCl_3) and PhSiH_3 (60 mM in CDCl_3) were cooled to 0 $^\circ\text{C}$. The precooled catalyst solution (0.4 mL, 2 μmol) was added to the vial followed by the addition of the precooled silane solution (0.1 mL of a 60 mM solution in CDCl_3 , 6 μmol) at 0 $^\circ\text{C}$ and stirred for 6 hrs. After the reaction had finished, tert-butyl isocyanide (approximately 6 μL , >20 equiv. to catalyst) was added and the mixture was shaken to quench the reaction. 1,4-Bis(trifluoromethyl)benzene (7.8 μL , 0.050 mmol) was used as an internal standard. ^1H NMR analysis revealed 85% of 2-methyl-2-pentene and 8% of 2-methyl-1-pentene. This product is known.⁷

^1H NMR (500 MHz, CDCl_3 , ppm) δ **5.14 – 5.08 (m, 1H)**, 1.98 (p, $^3J_{\text{HH}} = 7.4$ Hz, 2H), 1.68 (s, 3H), 1.60 (s, 3H), 0.97 – 0.89 (m, 3H).

Prop-1-en-1-ylbenzene (Table 1, Entry 4)

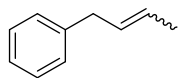


Allylbenzene (26.5 μL , 0.200 mmol) and NaBARF (7.0 mg, 8.0 μmol) were added to a 2-dram vial with a screw cap (PTFE/Liner) equipped with a magnetic stir bar.

Freshly prepared solutions of catalyst **12** (5 mM in CDCl₃) and PhSiH₃ (60 mM in CDCl₃) were cooled to 0 °C. The precooled catalyst solution (0.4 mL, 2 μmol) was added to the vial followed by the addition of the precooled silane solution (0.1 mL of a 60 mM solution in CDCl₃, 6 μmol) at 0 °C and stirred for 6 hrs. After the reaction had finished, tert-butyl isocyanide (approximately 6 μL, >20 equiv. to catalyst) was added and the mixture was shaken to quench the reaction. Pyridine (8.1 μL, 0.10 mmol) was used as an internal standard. ¹H NMR analysis revealed 93% of prop-1-en-1-ylbenzene (*E*:*Z* = 14.2/1). This product is known.¹⁰

¹H NMR (500 MHz, CDCl₃, ppm) δ 7.39 – 7.06 (m, 5H, *E* and *Z* signals overlap), 6.42 (m, 1H, *E* and *Z* signals overlap), 6.25 (m, 1H, *E* and *Z* signals overlap), **1.92 (*Z*, dd, ³*J*_{HH} = 7.2, ⁴*J*_{HH} = 1.9 Hz, 3H)**, **1.89 (*E*, dd, ³*J*_{HH} = 6.6, ³*J*_{HH} = 1.7 Hz, 3H)**.

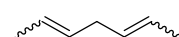
But-2-en-1-ylbenzene (Table 1, Entry 5)



But-3-en-1-ylbenzene (30.0 μL, 0.200 mmol) and NaBARF (7.0 mg, 8.0 μmol) were added to a 2-dram vial with a screw cap (PTFE/Liner) equipped with a magnetic stir bar. Freshly prepared solutions of catalyst **12** (5 mM in CDCl₃) and PhSiH₃ (60 mM in CDCl₃) were cooled to 0 °C. The precooled catalyst solution (0.4 mL, 2 μmol) was added to the vial followed by the addition of the precooled silane solution (0.1 mL of a 60 mM solution in CDCl₃, 6 μmol) at 0 °C and stirred for 8 hrs. After the reaction had finished, tert-butyl isocyanide (approximately 6 μL, >20 equiv. to catalyst) was added and the mixture was shaken to quench the reaction. Pyridine (8.1 μL, 0.10 mmol) was used as an internal standard. ¹H NMR analysis revealed 78% of but-2-en-1-ylbenzene (*E*:*Z* = 3.7/1) and 6% of but-1-en-1-ylbenzene. This product is known.⁹

¹H NMR (500 MHz, CDCl₃, ppm) δ 7.40 – 7.13 (m, 5H, *E* and *Z* signals overlaps with added pyridine), 5.68 – 5.48 (m, 2H, *E* and *Z* signals overlap), 3.43 (*Z*, d, ³*J*_{HH} = 5.1 Hz, 2H), 3.34 (*E*, d, ³*J*_{HH} = 6.5 Hz, 2H), **1.75 (*Z*, d, ³*J*_{HH} = 5.1 Hz, 1H)**, **1.71 (*E*, dd, ³*J*_{HH} = 6.1, ³*J*_{HH} = 1.4 Hz, 1H)**.

Hepta-2,5-diene (Table 1, Entry 6)

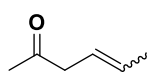


Hepta-1,7-diene (27 μL, 0.20 mmol) and NaBARF (7.0 mg, 8.0 μmol) were added to a 2-dram vial with a screw cap (PTFE/Liner) equipped with a magnetic stir bar. Freshly prepared solutions of catalyst **12** (5 mM in CDCl₃) and PhSiH₃ (60 mM in CDCl₃) were cooled to 0 °C. The

precooled catalyst solution (0.4 mL, 2 μ mol) was added to the vial followed by the addition of the precooled silane solution (0.1 mL of a 60 mM solution in CDCl_3 , 6 μ mol) at 0 °C and stirred for 45 min. After the reaction had finished, tert-butyl isocyanide (approximately 6 μ L, >20 equiv. to catalyst) was added and the mixture was shaken to quench the reaction. 1,4-Bis(trifluoromethyl)benzene (7.8 μ L, 0.050 mmol) was used as an internal standard. ^1H NMR analysis revealed 40% of hepta-2,5-diene ($E:Z = 1.5/1$). The remaining material appears to be hepta-1,5-diene. Hepta-2,5-diene is known.¹¹

^1H NMR (500 MHz, CDCl_3) δ 5.55 – 5.21 (m, 4H, E and Z signals overlap), **2.73 (E, m, 2H)**, **2.65 (Z, m, 2H)**, 1.68 – 1.55 (m, 6H, E and Z signals overlap).

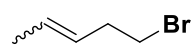
4-Hexen-2-one (Table 1, Entry 7)



5-Hexen-2-one (23.2 μ L, 0.200 mmol) and NaBARF (7.0 mg, 8.0 μ mol) were added to a 2-dram vial with a screw cap (PTFE/Liner) equipped with a magnetic stir bar. Freshly prepared solutions of catalyst **12** (5 mM in CDCl_3) and PhSiH_3 (60 mM in CDCl_3) were cooled to 0 °C. The precooled catalyst solution (0.4 mL, 2 μ mol) was added to the vial followed by the addition of the precooled silane solution (0.1 mL of a 60 mM solution in CDCl_3 , 6 μ mol) at 0 °C and stirred for 6 hrs. After the reaction had finished, tert-butyl isocyanide (approximately 6 μ L, >20 equiv. to catalyst) was added and the mixture was shaken to quench the reaction. 1,4-Bis(trifluoromethyl)benzene (7.8 μ L, 0.050 mmol) was used as internal standard. ^1H NMR analysis revealed 91% of 4-hexen-2-one ($E:Z = 2.4/1$) and 4% of 3-hexen-2-one. This product is known.⁸

^1H NMR (500 MHz, CDCl_3 , ppm) δ 5.71 – 5.45 (m, 2H, E and Z signals overlap), **3.15 (Z, d, $^3J_{\text{HH}} = 7.2$ Hz, 2H)**, **3.07 (E, d, $^3J_{\text{HH}} = 5.8$ Hz, 2H)**, 2.13 (E, s, 3H), 2.11 (Z, s, 3H), 1.67 (Z, d, $^3J_{\text{HH}} = 4.9$ Hz, 3H), 1.60 (E, d, $^3J_{\text{HH}} = 7.0$ Hz, 3H).

5-Bromo-2-pentene (Table 1, Entry 8)

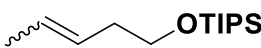


Catalyst **12** (1.7 mg, 2.0 μ mol) and NaBARF (7.0 mg, 8.0 μ mol) were added to a 2-dram vial. 5-Bromo-1-pentene (23.6 μ L, 0.200 mmol) was dissolved in CDCl_3 (0.4 mL). The vial was cooled to 0 °C and 0.1 mL of olefin solution was added followed by PhSiH_3 in CDCl_3 (0.1 mL of 60 mM solution, 6 μ mol). After five minutes of stirring the remaining 0.3 mL of olefin

solution was added. The mixture was stirred for 8 hours at 0 °C. After the reaction was finished, tert-butyl isocyanide (approximately 6 μ L, >20 equiv to catalyst) was added and the mixture was shaken to quench the reaction. 1,4-Bis(trifluoromethyl)benzene (7.8 μ L, 0.050 mmol) was used as an internal standard. ^1H NMR analysis revealed 64% of 5-bromo-2-pentene ($E:Z = 1.9/1$) and 17% of 5-bromo-1-pentene. This product is known.¹³

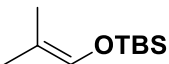
^1H NMR (500 MHz, CDCl_3 , ppm) δ 5.66 – 5.49 (m, 1H, E and Z signals overlap), 5.47 – 5.35 (m, 1H, E and Z signals overlap), 3.38 – 3.33 (m, 2H, E and Z signals overlap), **2.62 (Z, q, $^3J_{\text{HH}} = 7.7$ Hz, 2H)**, **2.53 (E, q, $^3J_{\text{HH}} = 7.0$ Hz, 2H)**, 1.67 (E, dd, $^3J_{\text{HH}} = 6.4$, $^4J_{\text{HH}} = 1.4$ Hz, 3H), 1.63 (Z, dd, $^3J_{\text{HH}} = 6.9$, $^4J_{\text{HH}} = 1.2$ Hz, 3H).

Triisopropyl(pent-3-enyloxy)silane (Table 1, Entry 9)

 Catalyst **12** (1.7 mg, 2.0 μ mol) and NaBARF (7.0 mg, 8.0 μ mol) were added to a 2-dram vial. Triisopropyl(pent-1-enyloxy)silane (48.0 mg, 0.200 mmol) was dissolved in CDCl_3 (0.4 mL). The vial was cooled to 0 °C and about a quarter of olefin solution (0.1 mL) was added followed by PhSiH_3 in CDCl_3 (0.1 mL of 60 mM solution, 0.006 mmol). After five minutes of stirring the remaining olefin solution (0.3 mL) was added. The mixture was stirred for 4 hours at 0 °C. After the reaction had finished, tert-butyl isocyanide (approximately 6 μ L, >20 equiv to catalyst) was added and the mixture was shaken to quench the reaction. 1,4-Bis(trifluoromethyl)benzene (7.8 μ L, 0.050 mmol) was used as an internal standard. ^1H NMR analysis revealed formation of 59% of triisopropyl(pent-3-enyloxy)silane ($E:Z = 3.8/1$). This product is known.¹⁴

^1H NMR (500 MHz, CDCl_3 , ppm) δ 5.60 – 5.35 (m, 2H), 3.68-3.71 (m, 2H, E and Z signals overlap), **2.32 (Z, q, $^3J_{\text{HH}} = 7.1$ Hz, 2H)**, **2.27 – 2.20 (E, m, 2H)**, 1.67 – 1.61 (m, 3H, E and Z signals overlap), 1.12 – 1.01 (m, 21H, E and Z signals overlap).


tert-Butyldimethyl((2-methylprop-1-en-1-yl)oxy)silane (Table 1, Entry 10)

 Tertbutyldimethyl((2-methylallyl)oxy)silane (37.0 mg, 0.200 mmol) and NaBARF (7.0 mg, 8.0 μ mol) were added to a 2-dram vial with a screw cap (PTFE/Liner) equipped with a magnetic stir bar. Freshly prepared solutions of catalyst **12** (5 mM in CDCl_3) and PhSiH_3 (60 mM in CDCl_3) were cooled to 0 °C. The precooled catalyst solution (0.4 mL, 2 μ mol) was added to the vial followed by the addition of the precooled silane solution (0.1 mL of a 60

mM solution in CDCl₃, 6 μmol) at 0 °C and stirred for 8 hrs. After the reaction had finished, tert-butyl isocyanide (approximately 6 μL, >20 equiv. to catalyst) was added and the mixture was shaken to quench the reaction. 1,4-Bis(trifluoromethyl)benzene (7.8 μL, 0.050 mmol) was used as an internal standard. ¹H NMR analysis revealed 55% of tert-butyldimethyl((2-methylprop-1-en-1-yl)oxy)silane and 33 % of tertbutyldimethyl((2-methylallyl)oxy)silane. This product is known.⁴


¹H NMR (500 MHz, CDCl₃, ppm) δ **6.03 (s, 1H)**, 1.59 (s, 3H), 1.53 (s, 3H), 0.92 (s, 9H), 0.10 (s, 6H).

tert-Butyldimethyl(prop-1-en-1-yloxy)silane (Table 1, Entry 11)

 **OTBS** (Allyloxy)(tert-butyl)dimethylsilane (35.0 mg, 0.200 mmol) and NaBARF (7.0 mg, 8.0 μmol) were added to a 2-dram vial with a screw cap (PTFE/Liner) equipped with a magnetic stir bar. Freshly prepared solutions of catalyst **12** (5 mM in CDCl₃) and PhSiH₃ (60 mM in CDCl₃) were cooled to 0 °C. The precooled catalyst solution (0.4 mL, 2 μmol) was added to the vial followed by the addition of the precooled silane solution (0.1 mL of a 60 mM solution in CDCl₃, 6 μmol) at 0 °C and stirred for 6 hrs. After the reaction had finished, tert-butyl isocyanide (approximately 6 μL, >20 equiv. to catalyst) was added and the mixture was shaken to quench the reaction. 1,4-Bis(trifluoromethyl)benzene (7.8 μL, 0.050 mmol) was used as an internal standard. ¹H NMR analysis revealed 73% of tert-butyldimethyl(prop-1-en-1-yloxy)silane (*E*:*Z* = 3.5/1) and 4% of (allyloxy)(tert-butyl)dimethylsilane. This product is known.⁴

¹H NMR (400 MHz, CDCl₃, ppm) δ 6.20 (m, 1H, *E* and *Z* signals overlap), **4.98 (*E*, dq, ³*J*_{HH} = 11.9, ³*J*_{HH} = 6.8 Hz, 1H)**, **4.55 – 4.41 (*Z*, m, 1H)**, 1.57 (*Z*, dd, ³*J*_{HH} = 6.7, ⁴*J*_{HH} = 1.7 Hz, 2H), 1.51 (*E*, dd, ³*J*_{HH} = 6.8, ⁴*J*_{HH} = 1.5 Hz, 1H), 0.92 (*Z*, s, 9H), 0.91 (*E*, s, 9H), 0.12 (*Z*, s, 6H), 0.12 (*E*, s, 6H).

Isomerization on Large Scale

 **OTBS** A flame-dried 200 mL round bottom flask in a nitrogen filled glovebox was charged with NaBARF (195 mg, 0.220 mmol). The flask was fitted with a rubber septum, taken out of glovebox, and cooled to 0 °C. Catalyst **12** (174 mg, 0.200 mmol) was added *via* syringe as a solution in CH₂Cl₂ (15 mL) followed by addition of allyloxy(tert-butyl)dimethylsilane (172 mg, 1.00 mmol) as a solution in CH₂Cl₂ (5 mL). Phenylsilane (65.0 mg, 0.600 mmol) was added *via* syringe. After stirring for 5 minutes, additional allyloxy(tert-butyl)dimethylsilane (3.27 g, 19.0

mmol) was added *via* syringe (for a total of 3.44 g of olefin). After 22 hours, a nBu_4NCl (2 mmol) solution in CH_2Cl_2 (10 mL) was added and solvent was gently evaporated on a rotovap. To the resulting residue hexanes (50 mL) was added to precipitate the catalyst. The mixture was filtered and the filtrate was distilled at 70 -72 °C/50 torr to afford 2.02 g (59%, $E:Z = 3.8/1$) of a product as a colorless oil.

^1H NMR (500 MHz, CDCl_3 , ppm) δ 6.20 (m, 1H, E and Z signals overlap), **4.98 (E, dq, $^3J_{\text{HH}} = 11.9$, $^3J_{\text{HH}} = 6.8$ Hz, 1H)**, **4.55 – 4.41 (Z, m, 1H)**, 1.57 (Z, dd, $^3J_{\text{HH}} = 6.7$, $^4J_{\text{HH}} = 1.7$ Hz, 2H), 1.51 (E, dd, $^3J_{\text{HH}} = 6.8$, $^4J_{\text{HH}} = 1.5$ Hz, 1H), 0.92 (Z, s, 9H), 0.91 (E, s, 9H), 0.12 (Z, s, 6H), 0.12 (E, s, 6H).

Isomerization of (1- ^{13}C)-1-Decene

Synthesis

To the suspension of $^{13}\text{CH}_3\text{PPh}_3\text{I}^{15}$ (2.49 g, 6.09 mmol) in dry THF (20 mL) a solution of NaHMDS (1.12 g, 6.09 mmol) in dry THF (6 mL) was added *via* canula at 0° C. The reaction mixture was stirred at 0° C for 40 min. Subsequently, nonaldehyde (0.670 g, 4.69 mmol) was added and the reaction was stirred at room temperature for 12 hours. An orange suspension formed. After completion (TLC control, SiO_2 , hexanes, $R_f = 1.0$, KMnO_4 stain), the reaction was diluted with pentane (30 mL) and solids were filtered off. The collected solids were washed with pentane (2×30 mL). Washings and filtrate were combined and washed with saturated NH_4Cl aqueous solution (50 mL) and water (50 mL). The organic phase was dried over MgSO_4 , filtered and concentrated in vacuo. The resulting oil was purified on a column (eluent pentane) to afford 0.24 g (36%) of a product as a colorless oil. Additional purification was necessary and part (0.07 g) of the product was stirred in pentane (10 mL) over chunks of sodium for 4 h recovering 0.05 g of 1-decene. ^1H -NMR analysis shows the presence of traces of 2-decene (~ 5% based on ^1H -NMR).

^1H NMR (600 MHz, CDCl_3 , ppm) δ 5.83 – 5.77 (m, 1H), 4.96 (ddd, $J = 156.0, 17.1, 1.6$ Hz, 1H), 4.90 (dd, $J = 156.0, 10.1$ Hz, 1H), 2.02 – 2.05 (m, 2H), 1.37 – 1.26 (m, 12H), 0.86 (t, $J = 7.0$ Hz, 3H).

Isomerization of (1- ^{13}C)-1-Decene

A 2-dram vial with a screw cap (PTFE/Liner) equipped with a magnetic stir bar was charged with NaBARF (7.0 mg, 8.0 μmol) and (1- ^{13}C)-1-decene (19 μL , 0.10 mmol). Freshly prepared solutions of catalyst (5 mM in CDCl_3) and PhSiH_3 (60 mM in CDCl_3) were cooled to 0 °C. The precooled catalyst solution (0.4 mL, 2 μmol) was added to the vial followed by the addition of the precooled silane solution (0.1 mL of a 60 mM solution in CDCl_3 , 6 μmol). The vial was sealed, put in a cooling bath at 0 °C and stirred for 8 hours. After the reaction was finished, tert-butyl isocyanide (approximately 6 μL , >20 equiv to catalyst) was added and the mixture was shaken to quench the reaction. Quantification was performed by ^1H NMR spectroscopy with peak identification performed by the large ^{13}C -H coupling. ^1H NMR analysis revealed 15% (1- ^{13}C)-1-decene, 75% (1- ^{13}C)-2-decene (E:Z = 1.8:1), and 10% other internal olefins.

^1H NMR (500 MHz, CDCl_3 , ppm) δ 5.53 – 5.25 (m, 2H), 2.09 – 1.90 (m, 2H), 1.64 (dd, $J = 125.4$, 4.4 Hz, 1H), 1.60 (Z, dd, $J = 125.6$, 6.1 Hz, 3H), 1.37 – 1.17 (m, 8H), 0.91 – 0.84 (m, 3H).

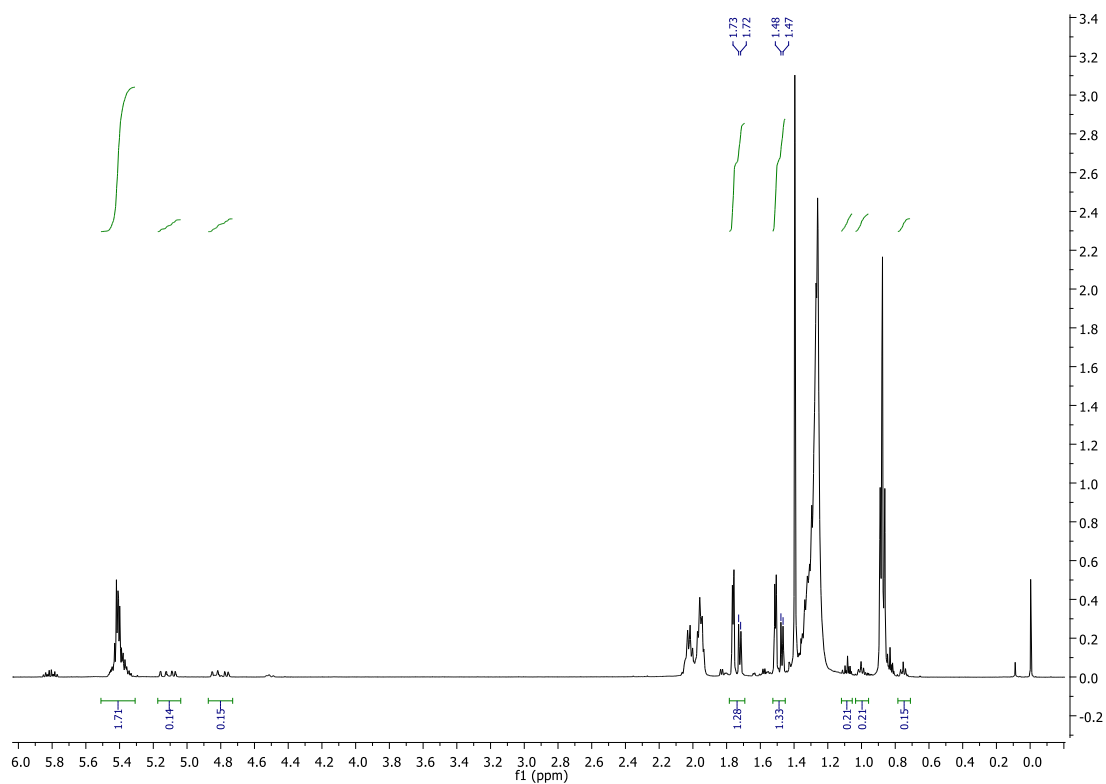
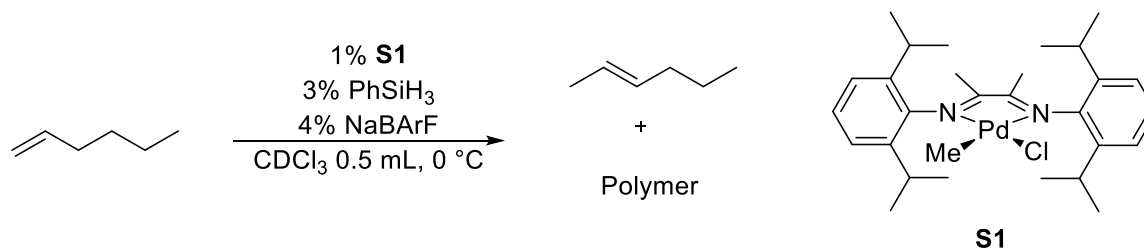


Figure S1: Reaction mixture of Isomerized (1- ^{13}C)-1-Decene.

Isomerization with a Standard Diimine Catalyst

A traditional palladium catalyst was tested for its activity toward isomerizing 1-hexene using the same conditions as the “sandwich” catalyst.

Scheme S1: Isomerization/Polymerization with Standard Diimine Catalyst



Isomerization/Polymerization of 1-Hexene Using Standard Catalyst

A 2-dram vial with a screw cap (PTFE/Liner) equipped with a magnetic stir bar was charged with NaBARF (7 mg, 8 μ mol) and 1-hexene (25 μ L, 0.2 mmol). Freshly prepared solutions of catalyst S1 (5 mM in CDCl₃) and PhSiH₃ (60 mM in CDCl₃) were cooled to 0 °C. The precooled catalyst solution (0.4 mL, 2 μ mol) was added to the vial followed by the addition of the precooled silane solution (0.1 mL of a 60 mM solution in CDCl₃, 6 μ mol). Sequence of addition is crucial for obtaining high yield. The vial was sealed, placed in a cooling bath at 0 °C and allowed to stir for both 1 hour and 3 hours. After the reaction had finished, tert-butyl isocyanide (approximately 6 μ L, >20 equiv. to catalyst) was added and the mixture was shaken to quench the reaction. The solution immediately turned from deep red to orange. An internal standard (1,4-bis(trifluoromethyl)benzene (7.8 μ L, 0.050 mmol) was added to the vial and the whole reaction mixture was transferred to an NMR tube.

Under the standard reaction conditions both the isomerization and polymerization of 1-hexene occurs and leads to the formation of internal hexenes along with higher order products. This can be seen by looking at the total integration of olefin signal which indicates the consumption of olefin (76% remaining at 1 hour, 65% remaining at 3 hours) and the formation of polymer.

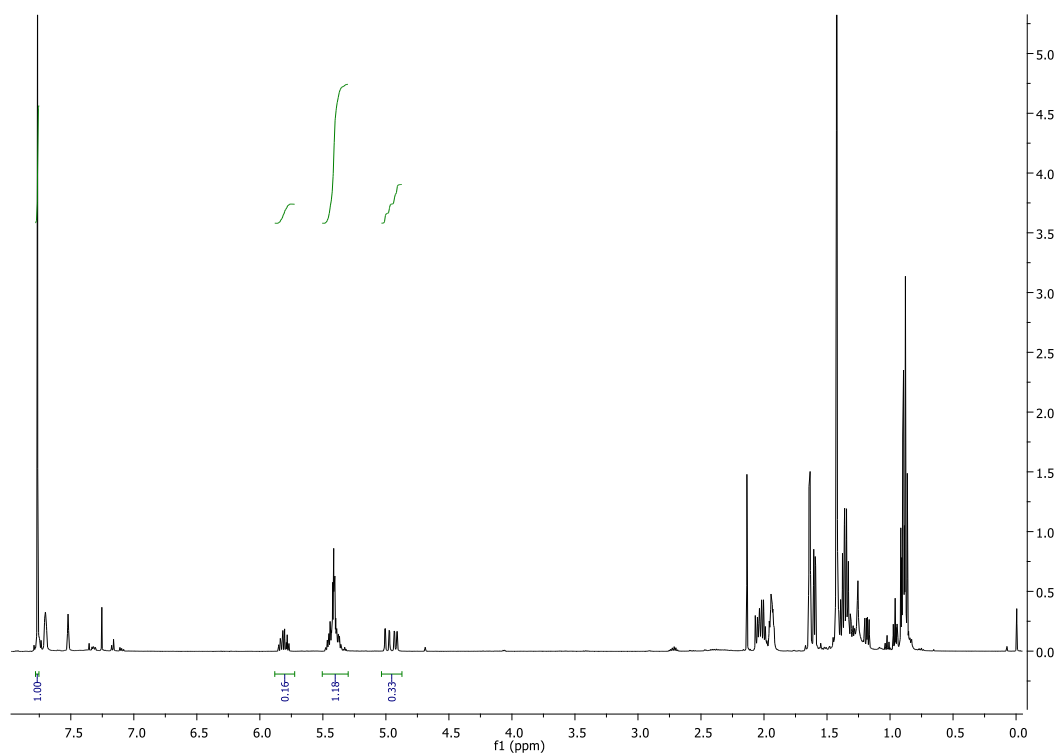


Figure S2. NMR Spectra of Isomerization of 1-hexene Using **S1** Showing Overall Consumption of Olefin after 1 Hour.

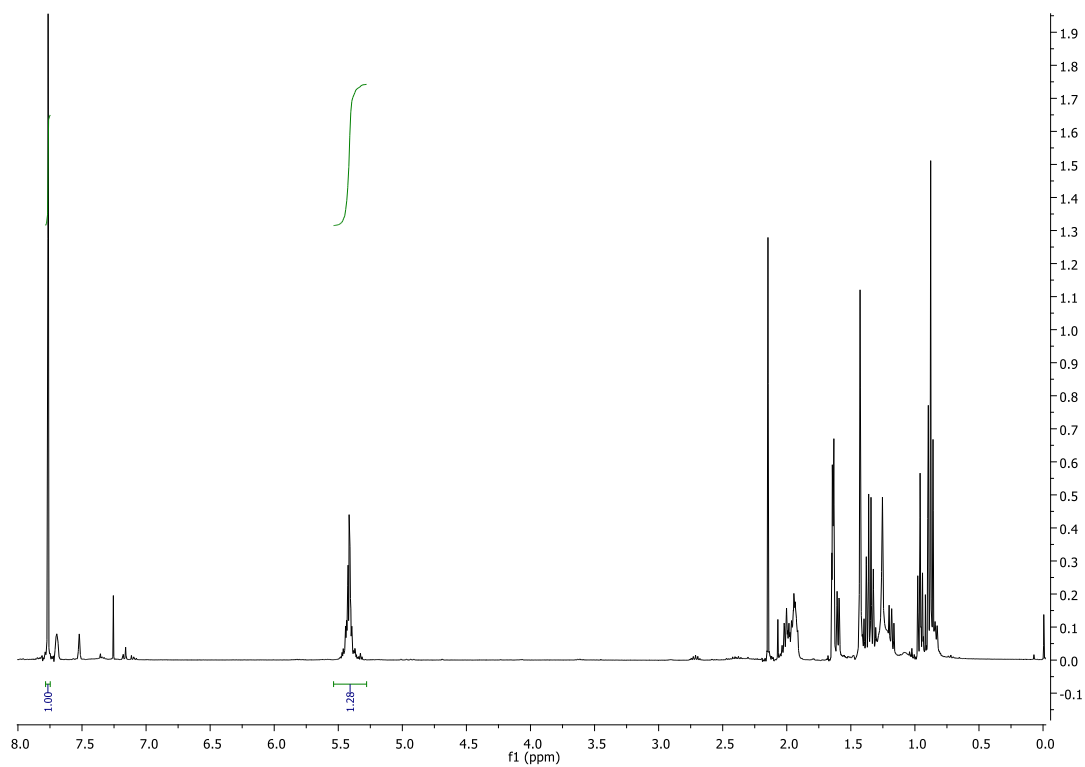


Figure S3. NMR Spectra of Isomerization of 1-hexene Using **S1** Showing Overall Consumption of Olefin after 3 Hours.

Low Temperature NMR Experiments

General comments on NMR experiments

All NMR experiments were performed on a JEOL EC-600 spectrometer using residual solvent peaks for reference. Samples were given at least five minutes to equilibrate at a given temperature before measurements were taken.

General Procedure for Low Temperature NMR Experiments

To screw capped NMR tube with a septa catalyst **12** (8.7 mg, 10 μ mol) was added. The NMR tube was flushed with nitrogen. In a nitrogen filled glovebox, NaBARF (9.7 mg, 11.0 μ mol) was added. The NMR tube was cooled to -78 °C in a dry ice/acetone bath. Olefin (0.10 mmol to 0.20 mmol) was added *via* syringe to the NMR tube followed by CD₂Cl₂ (0.8 mL) and the mixture was kept for at least 30 minutes at -78 °C. Phenylsilane (0.1 mmol to 0.20 mmol) and mesitylene (1.40 μ L, 10.0 μ mol) were then added *via* syringe. The NMR tube was transferred to a NMR probe precooled to -80 °C. The probe was then warmed to -55 °C for spectra acquisition.

Catalyst Activation and Insertion of Olefin

Catalyst activation by phenylsilane and olefin insertion was modeled as shown in Scheme S1. Only **S3** and **S7** are visible in the reaction mixture. By measuring the disappearance of the Pd-Me signal the rate of activation can be measured. Using pseudo-first order kinetics the rate can be modeled as equation **1** which can be measured using pseudo-first order kinetics. The concentration of silane and olefin were varied to show the effect on the measured rate in order to determine if the mechanistic scheme is consistent with experimental observations. Three experiments were conducted with varying concentrations as shown in Table S1. These showed that the reaction was inhibited by increased olefin and promoted by added concentration of silane as would be expected if equation **1** is correct.

$$(1) \quad rate = \frac{d[3]}{dt} = \frac{k_1}{k_{-1}} k_2 \frac{[PhSiH_3]}{[Olefin]}$$

Scheme S2. Proposed Mechanistic Route for Catalyst Activation

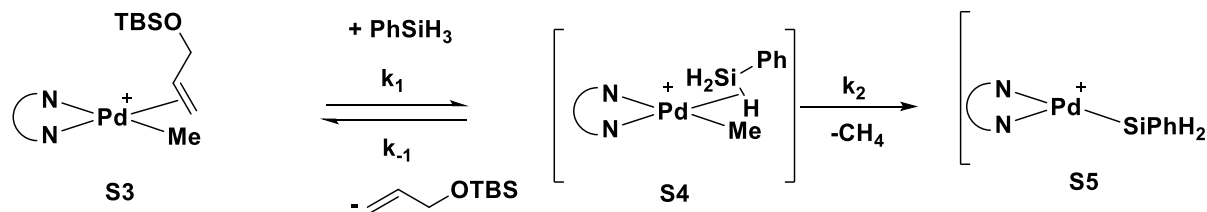


Table S1. Kinetic Data for Catalyst Activation

Equivalents of olefin	Equivalents of silane	Measured rate
10	10	$2.81 \times 10^{-4} \text{ s}^{-1} \pm 4.3 \times 10^{-5}$
10	20	$5.00 \times 10^{-4} \text{ s}^{-1} \pm 2.2 \times 10^{-5}$
20	10	$1.82 \times 10^{-4} \text{ s}^{-1} \pm 5.4 \times 10^{-6}$

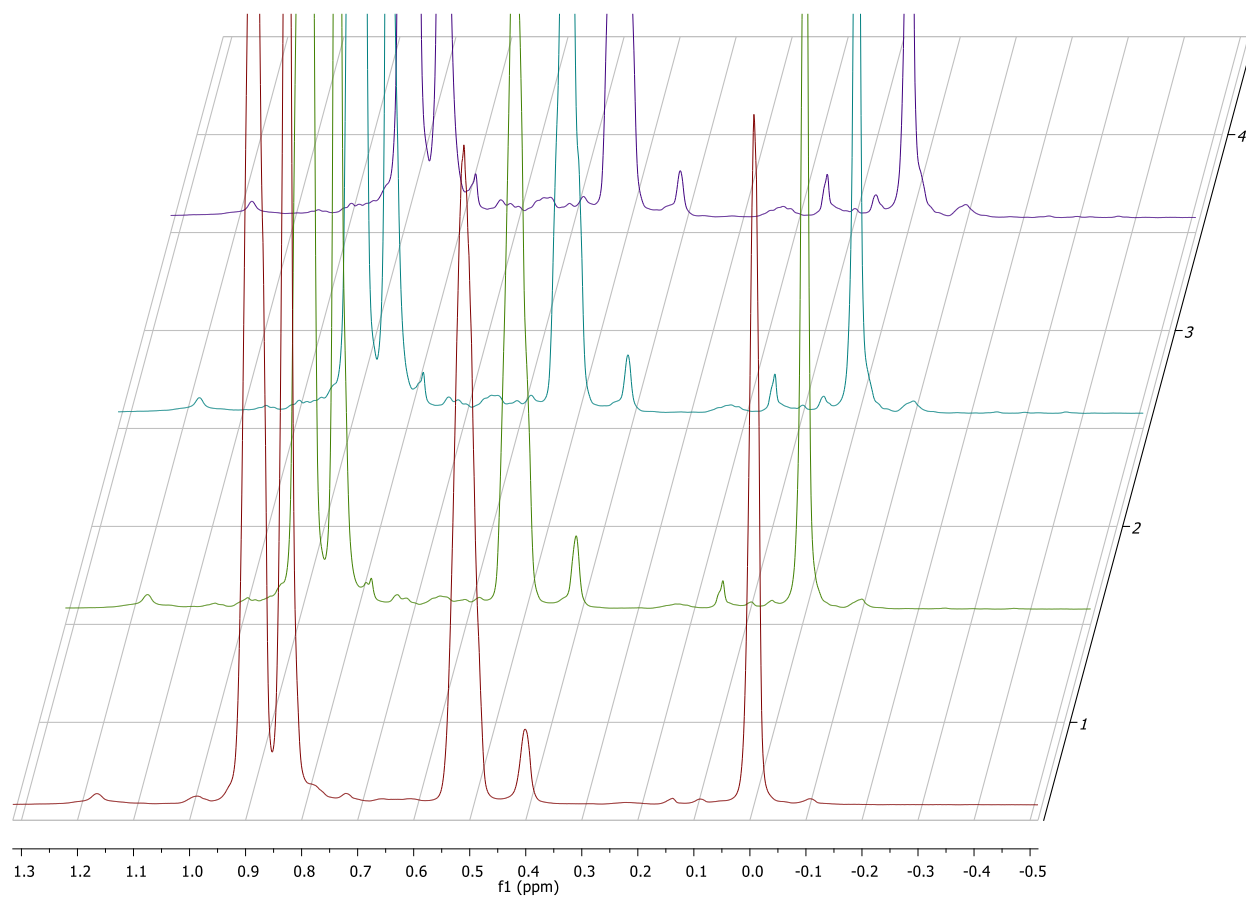


Figure S4. Sample NMR for measurement of consumption of Pd-Me signal (0.41 ppm) and formation of methane (0.19 ppm).

Kinetic Plots

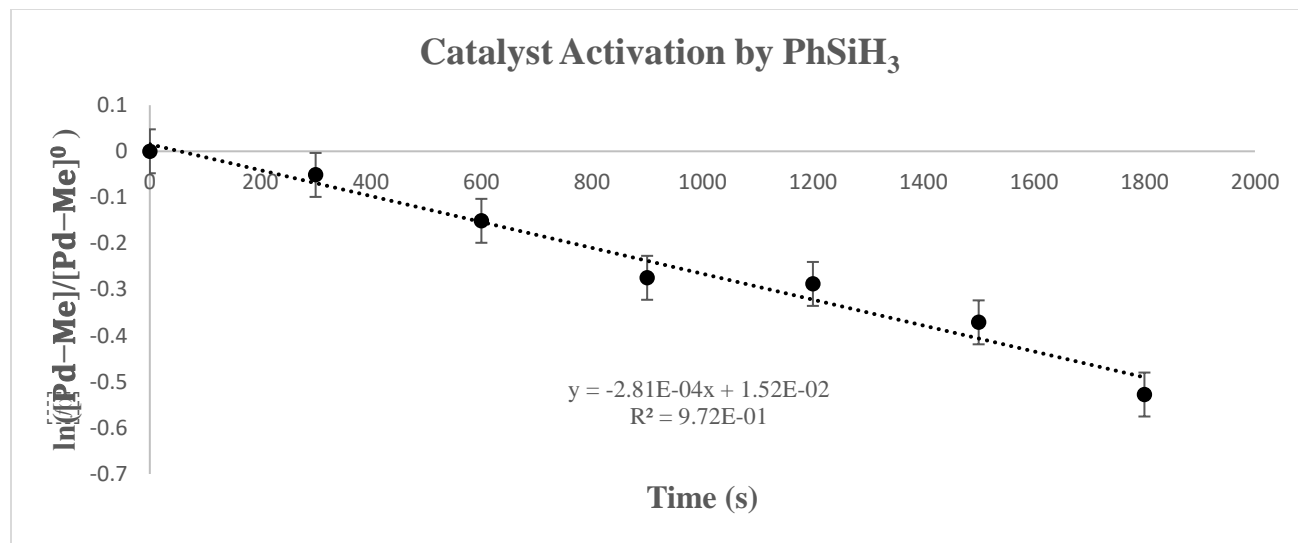


Figure S5. Kinetic plot for activation of catalyst with 10 equivalents of phenylsilane and 10 equivalents of olefin.

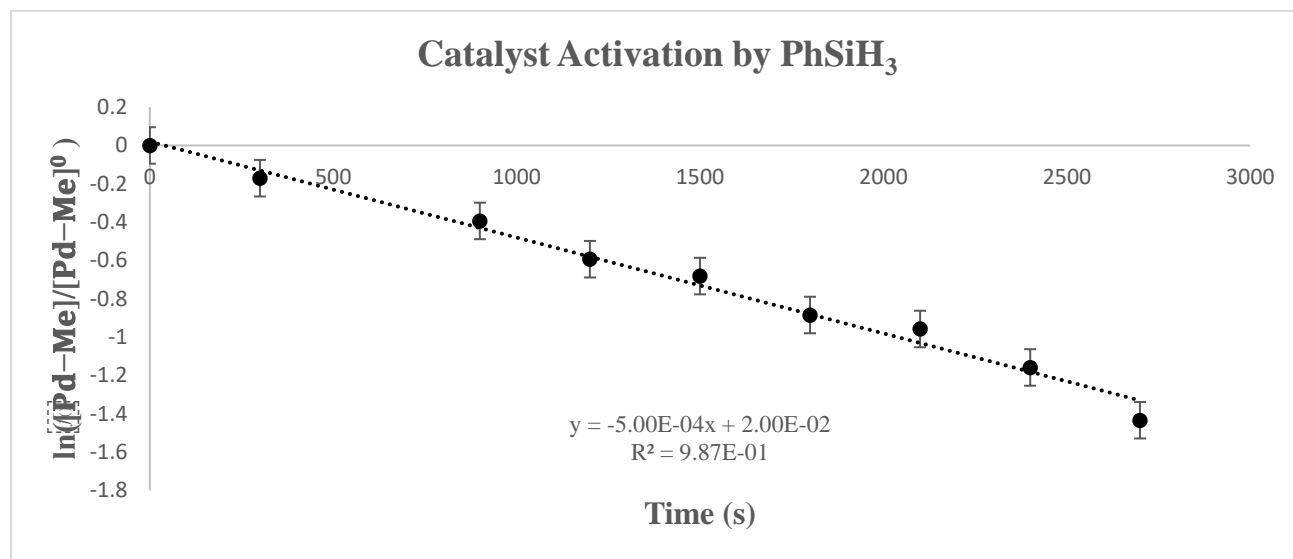


Figure S6. Kinetic plot for activation of catalyst with 10 equivalents of phenylsilane and 20 equivalents of olefin.

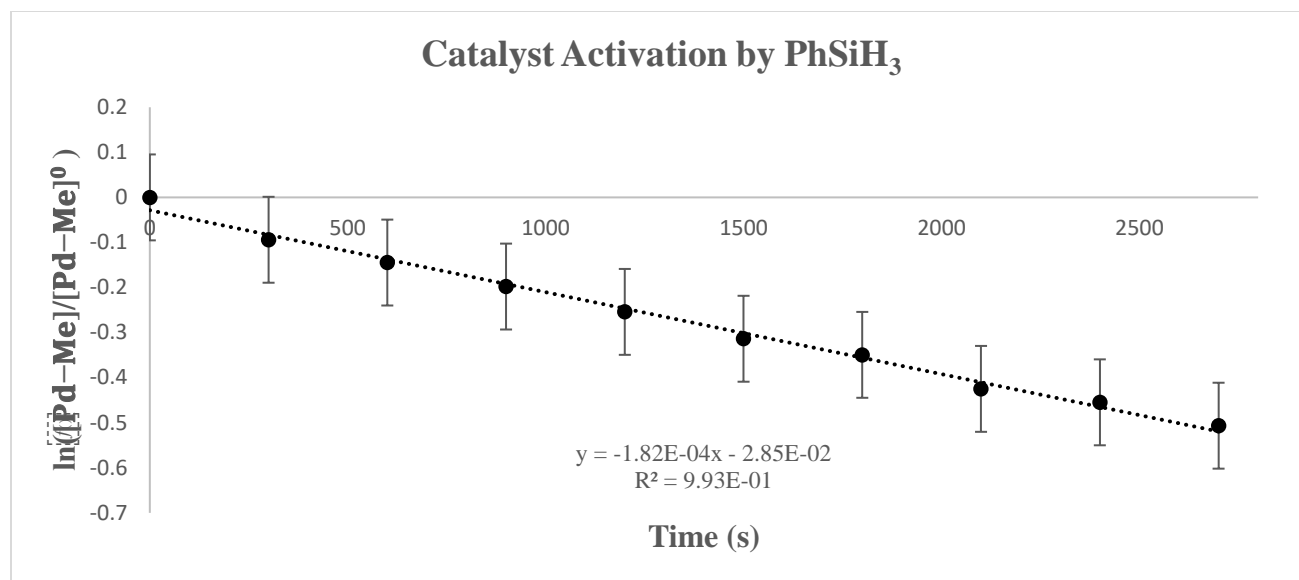


Figure S7. Kinetic plot for activation of catalyst with 20 equivalents of phenylsilane and 10 equivalents of olefin.

Initial 1-Hexene Isomerization Experiments

Synthesis of **11** and $[\text{H}(\text{OEt}_2)]^+[\text{BArF}]^-$ have been previously reported.⁵

Procedure for Initial Low Temperature Experiments

In a drybox under argon atmosphere, a screw-capped NMR tube was charged with **11** (6 mg, 0.009 mmol) and $[\text{H}(\text{OEt}_2)]^+[\text{BArF}]^-$ (9 mg, 0.009 mmol). The tube was then placed at $-78\text{ }^\circ\text{C}$ out of the glovebox and CD_2Cl_2 (0.6 mL) was added via gastight syringe, then it was briefly shaken to dissolve the palladium catalyst. 1-Hexene (*ca.* 15 eq.) was added to the $-78\text{ }^\circ\text{C}$ solution via gastight syringe and the NMR tube again shaken. The tube was transferred to the precooled NMR probe and spectra were acquired. The BArF signals at the ^1H NMR spectra were used as internal standards. The rate constants reported here are the averages of values obtained for at least two independent runs.

Initial Observation of 1-Hexene Isomerization

The isomerization of 1-hexene to yield *trans*-2-hexene as the major product (*ca.* 90 % of *trans*-2-hexene and 10 % of other minor isomers and polymer) was monitored by ^1H NMR spectroscopy by the disappearance of the olefinic proton signal at 5.85 ppm. Conversion to *trans*-2-hexene was determined by new growing peaks at 5.45 (m), 1.96 (m), 1.66 (s), 1.36 (apparent sextet, $^3J_{\text{HH}} = 7.8$ Hz) and 0.91 (t, $^3J_{\text{HH}} = 7.8$ Hz). Initial rates for isomerization were measured at 268 K with variable concentrations of 1-hexene (from 0.2 to 1.2 M). The isomerization was shown to be first order in 1-hexene. Polymerization of the olefin was monitored at room temperature by the disappearance of the olefinic ^1H NMR peak of *trans*-2-hexene at 5.45 ppm, showing a first order kinetic behaviour in olefin concentration. The first-order rate constant was shown to be $1.2 \cdot 10^{-4}\text{ s}^{-1}$ at $20\text{ }^\circ\text{C}$, which corresponds to a free energy of activation of ΔG^\ddagger of *ca.* $22.4\text{ kcal mol}^{-1}$.

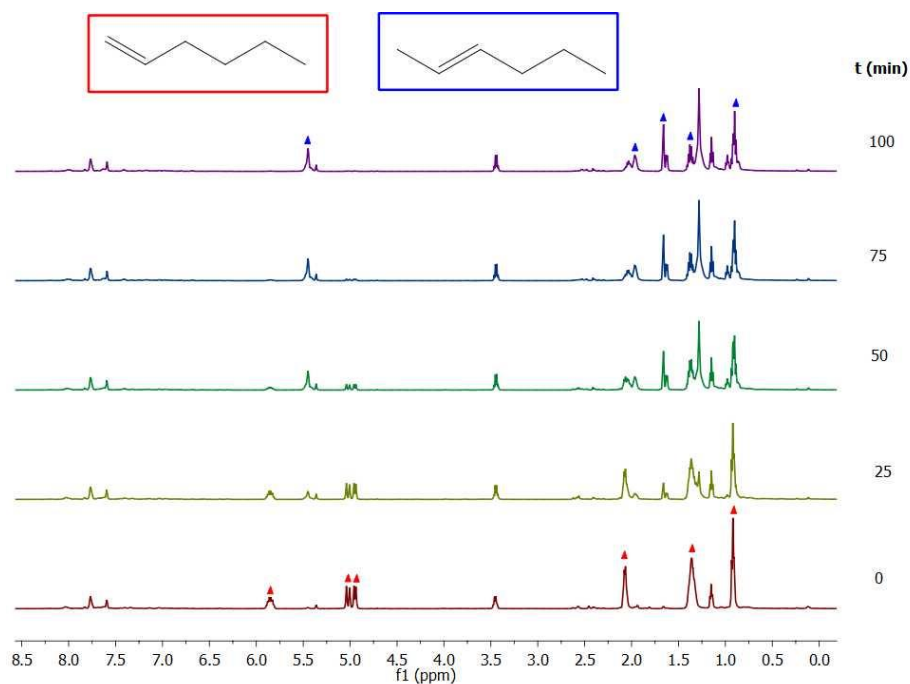


Figure S8: Isomerization of 1-hexene catalyzed by **11** monitored by ^1H NMR spectroscopy. Red peaks correspond to 1-hexene, whereas blue peaks indicate growing *trans*-2-hexene signals.

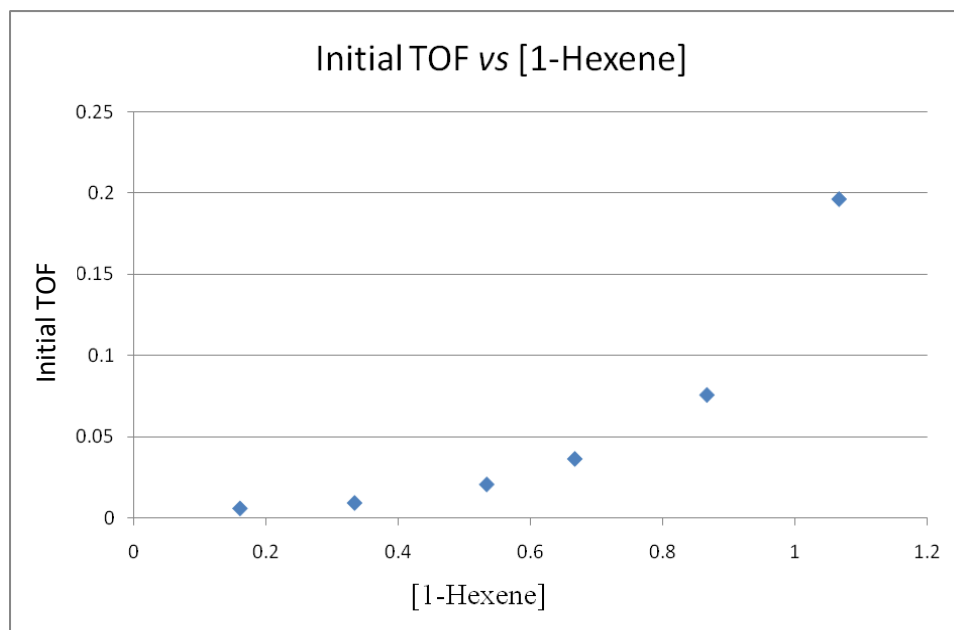


Figure S9: Dependence of the initial rate of 1-hexene consumption with respect to the initial concentration of 1-hexene.

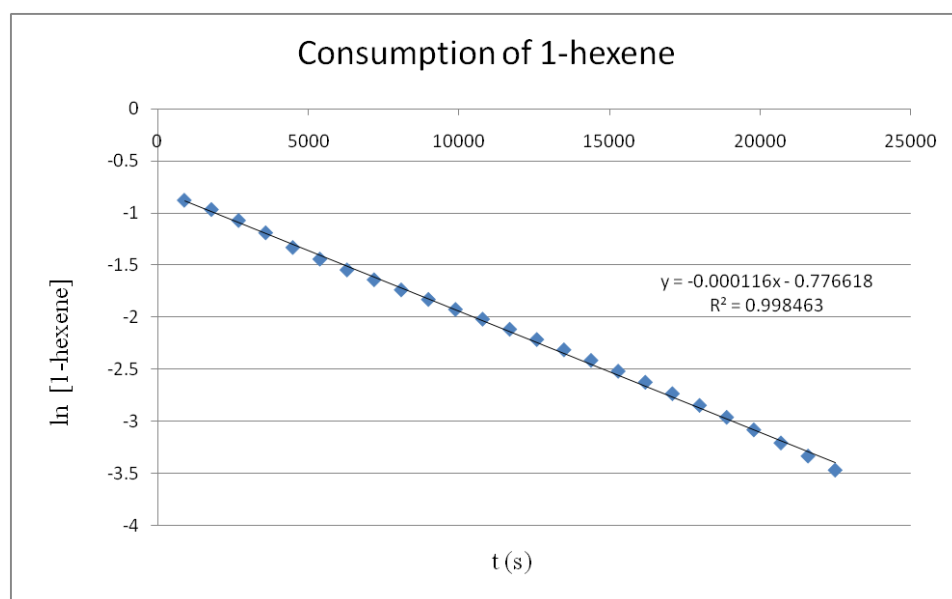


Figure S10: First-order consumption of 1-hexene at 20 °C.

Optimization of Temperature and Concentration Effects

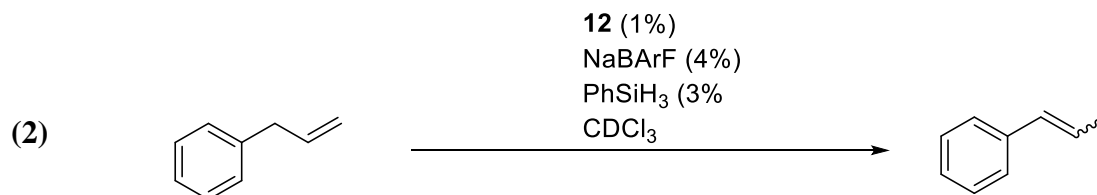


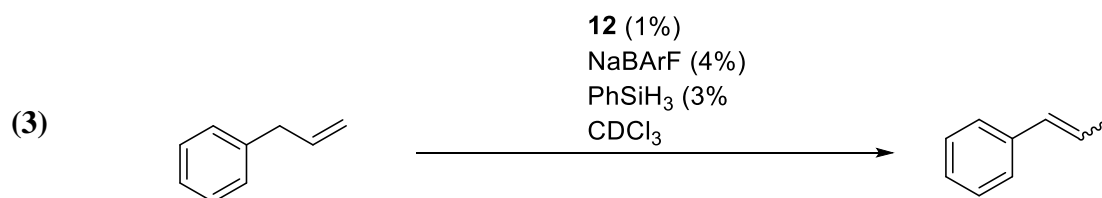
Table S2: Optimization of Temperature and Concentration

#	Concentration	Temperature	Yield	E:Z
1	0.4 M	0 °C	93%	14.2:1
2	0.2 M	0 °C	16%	4.7:1
3	0.4 M	-30 °C	24%	5.3:1
4	0.4 M	RT	94%	12.3:1

Allylbenzene (26.5 μL , 0.200 mmol) and NaBARF (7.0 mg, 8.0 μmol) were added to a 2-dram vial with a screw cap (PTFE/Liner) equipped with a magnetic stir bar. Freshly prepared solutions of catalyst **12** (5 mM in CDCl_3) and PhSiH_3 (60 mM in CDCl_3) were cooled to the indicated temperature. The precooled catalyst solution (0.4 mL, 2 μmol) was added to the vial followed by the addition of the precooled silane solution (0.1 mL of a 60 mM solution in CDCl_3 , 6 μmol) at the indicated temperature. Excess CDCl_3 was added as need to dilute the reaction to the desired concentration and then the mixture was stirred for 6 hrs. After the reaction had finished, tert-butyl isocyanide (approximately 6 μL , >20 equiv to catalyst) was added and the mixture was shaken to quench the reaction. 1,4-Bis(trifluoromethyl)benzene (7.8 μL , 0.050 mmol) was used as an internal standard.

Yield Measurement via Gas Chromatography

In order to confirm that NMR measurements were sufficiently accurate to determine yield, gas chromatography was used as well. Gas Chromatography was performed on a Shimadzu GC-2010 Gas Chromatograph. Injection temperature was 250 °C. The temperature program was as follows. Hold 40 °C for 5 minutes. Ramp to 150 °C at 5 °C/min. Ramp to 250 °C at 40 °C/min. Hold at 250 °C for 1 minutes. The detector was at 280 °C. Response factors were calculated using standards.



Allylbenzene (26.5 μ L, 0.200 mmol) and NaBARF (7.0 mg, 8.0 μ mol) were added to a 2-dram vial with a screw cap (PTFE/Liner) equipped with a magnetic stir bar. Freshly prepared solutions of catalyst **12** (5 mM in CDCl₃) and PhSiH₃ (60 mM in CDCl₃) were cooled to the indicated temperature. The precooled catalyst solution (0.4 mL, 2 μ mol) was added to the vial followed by the addition of the precooled silane solution (0.1 mL of a 60 mM solution in CDCl₃, 6 μ mol) at the indicated temperature. Excess CDCl₃ was added to dilute the reaction to the desired concentration and then the mixture was stirred for 6 hrs. After the reaction had finished, it was diluted with CH₂Cl₂ (0.5 mL) and injected directly into the GC. Calculated yield 88% (E:Z 14.5:1) which corresponds well with yield obtained by NMR analysis.

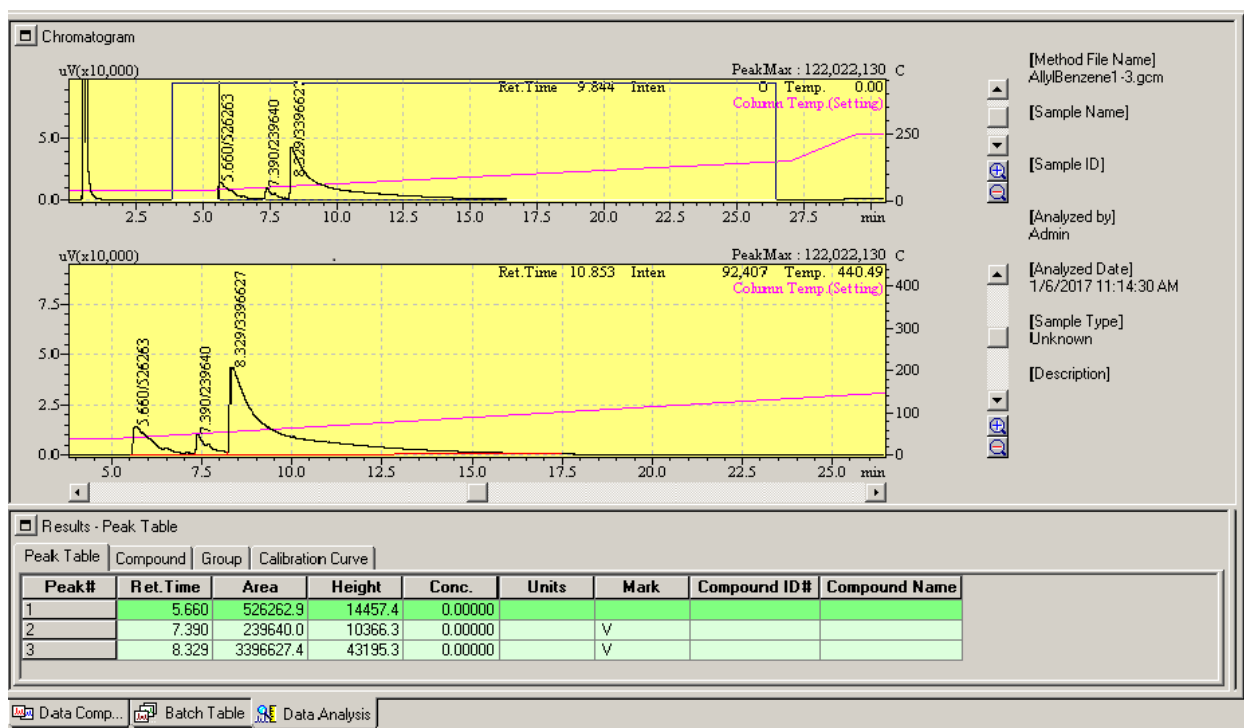
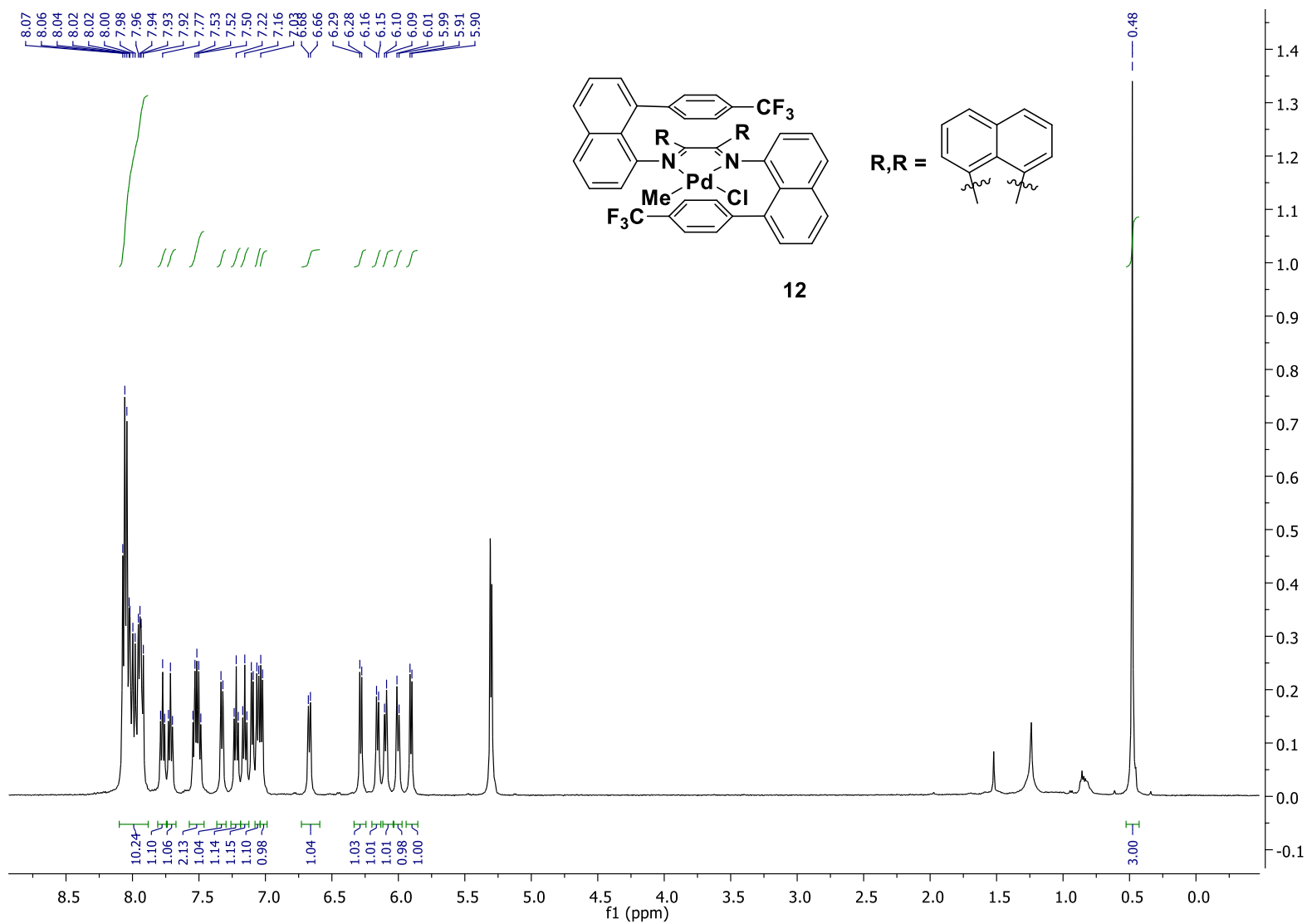
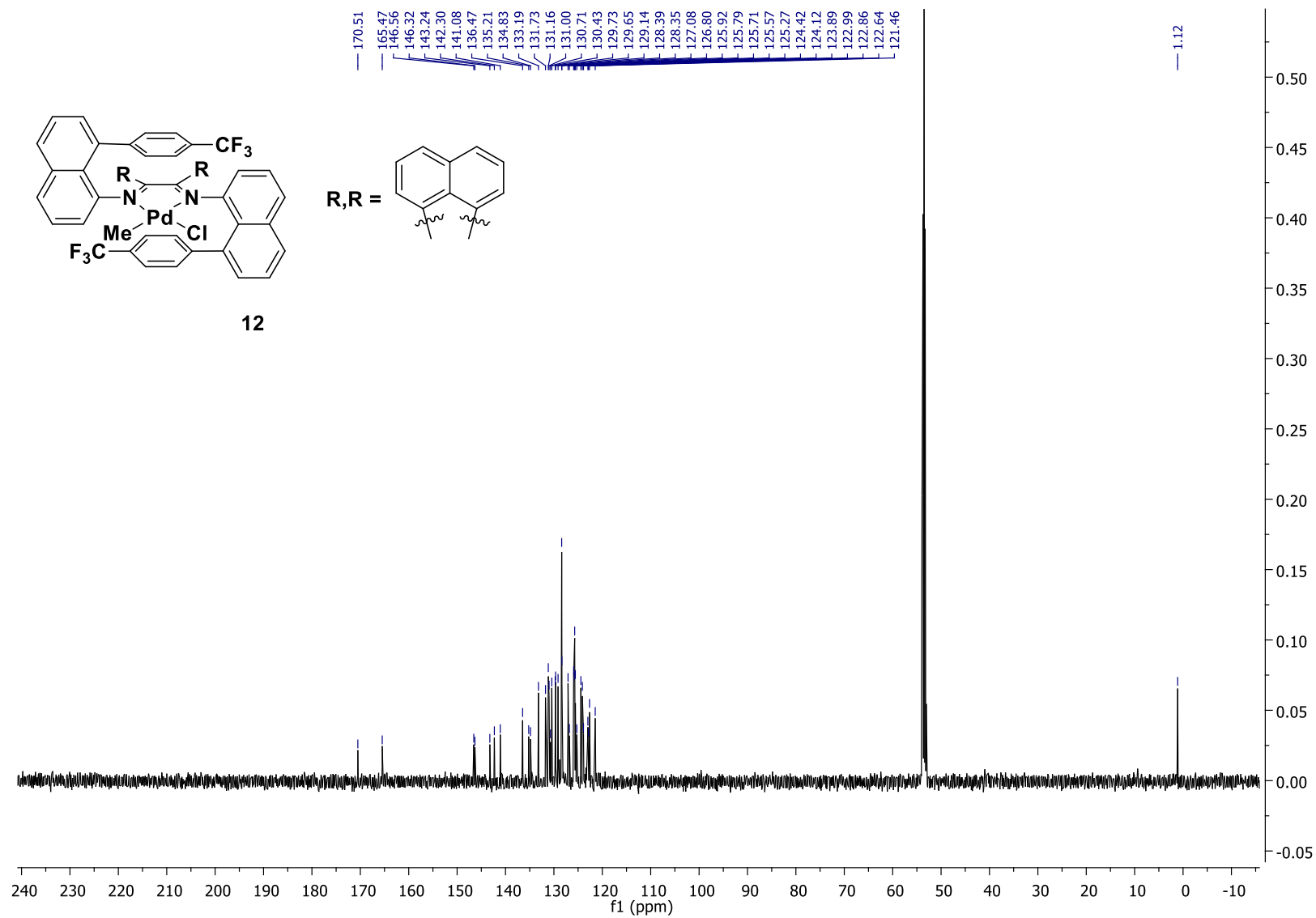


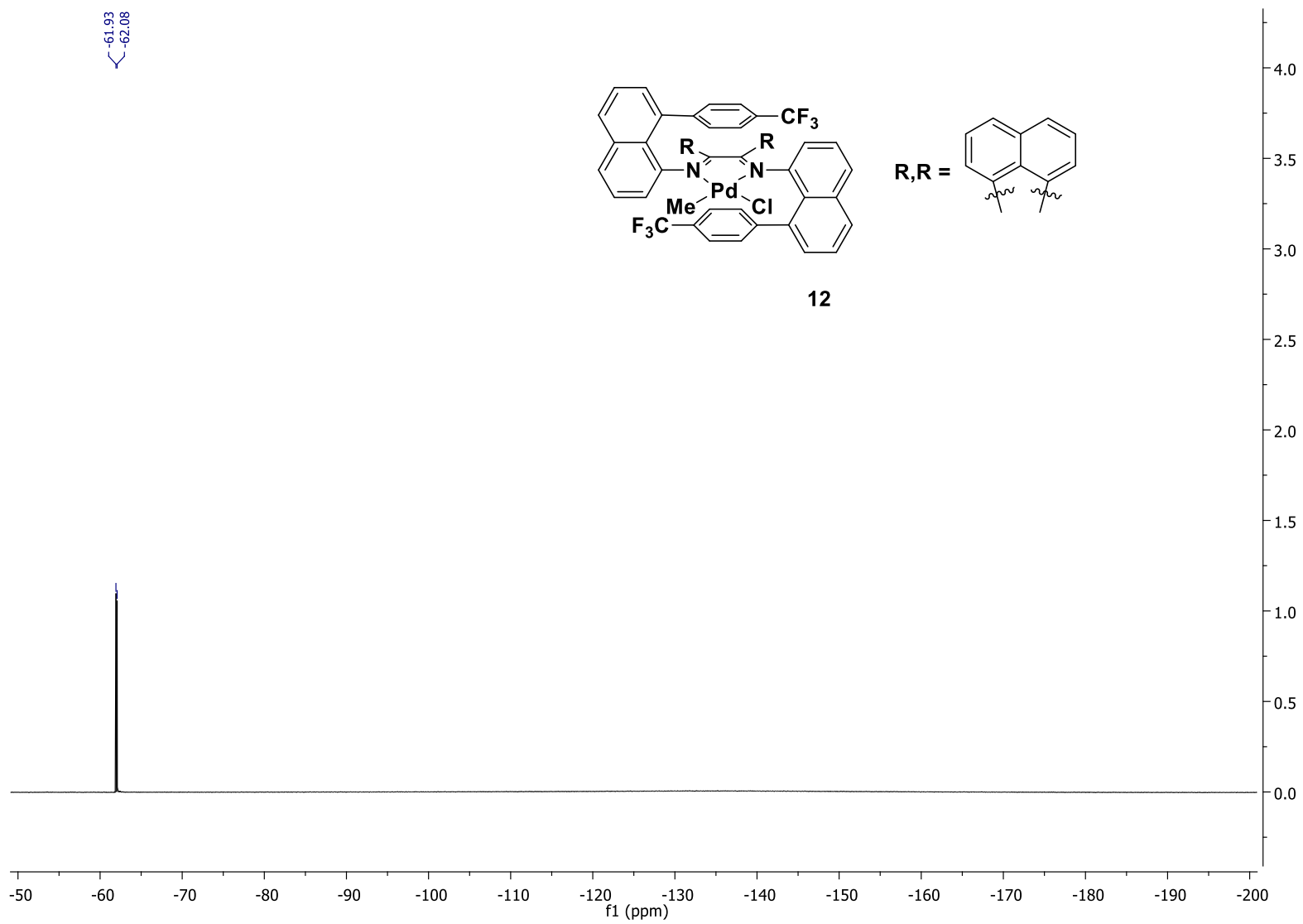
Figure S11: Sample GC Chromatogram of Crude Isomerization Reaction

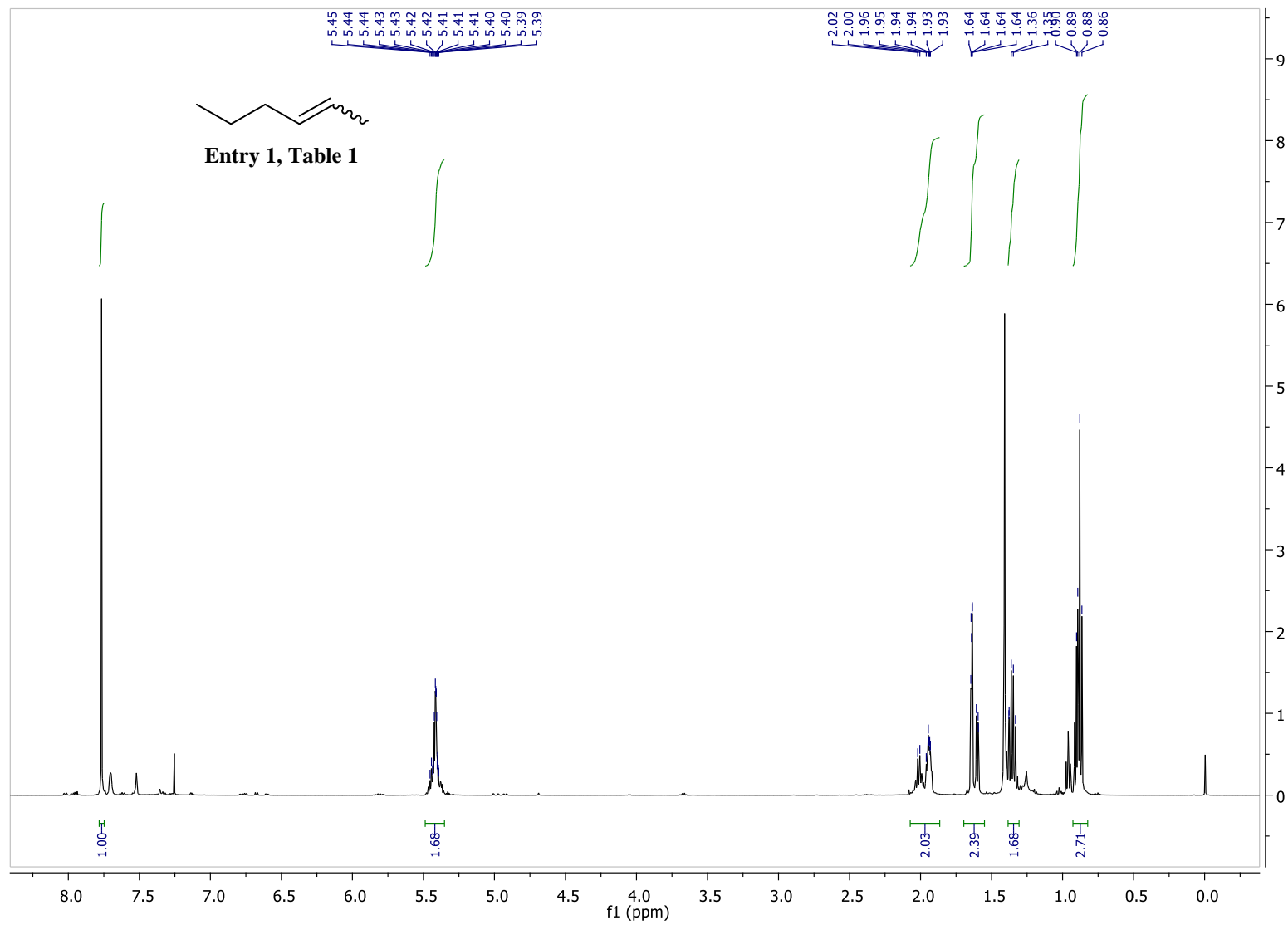
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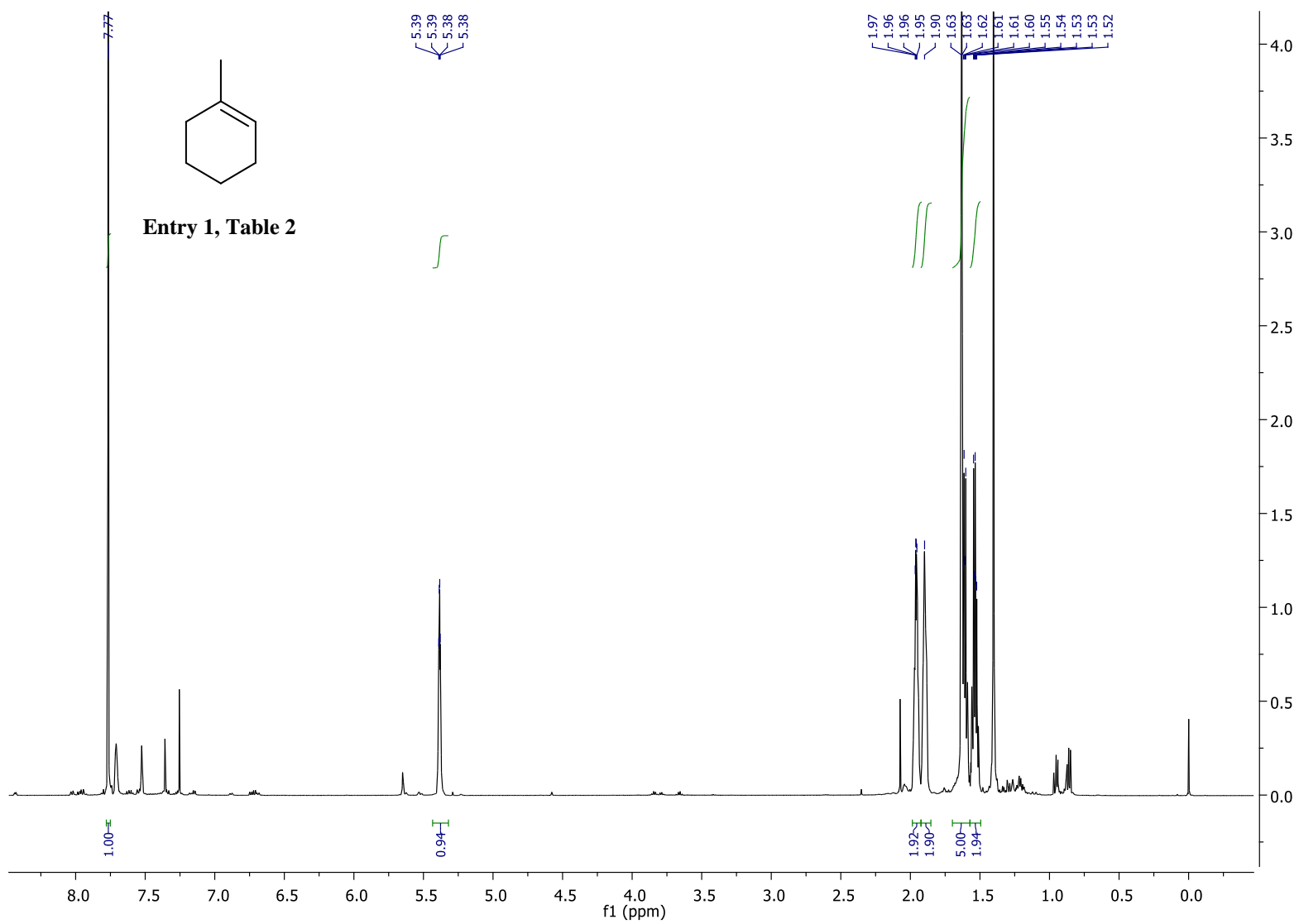
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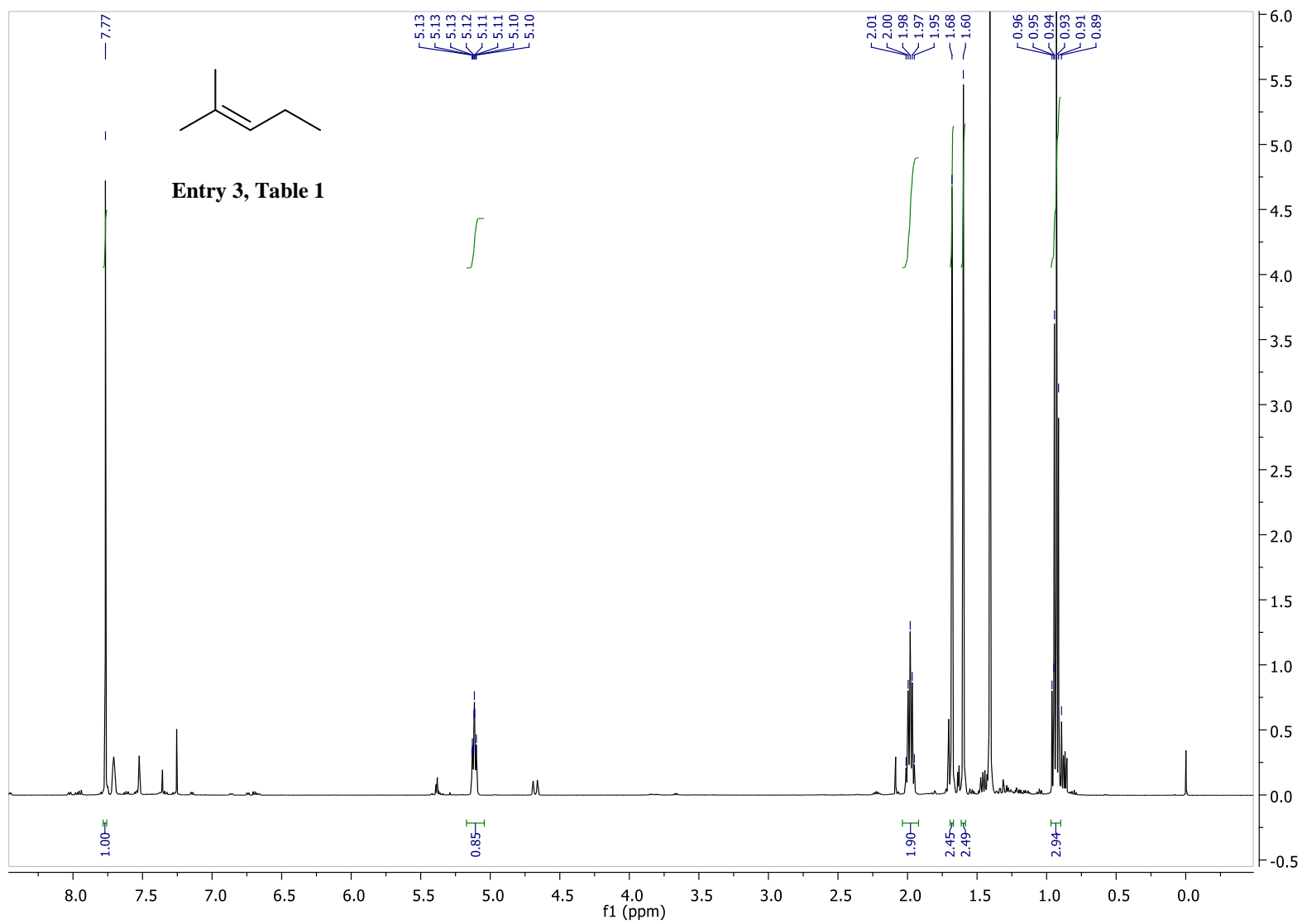


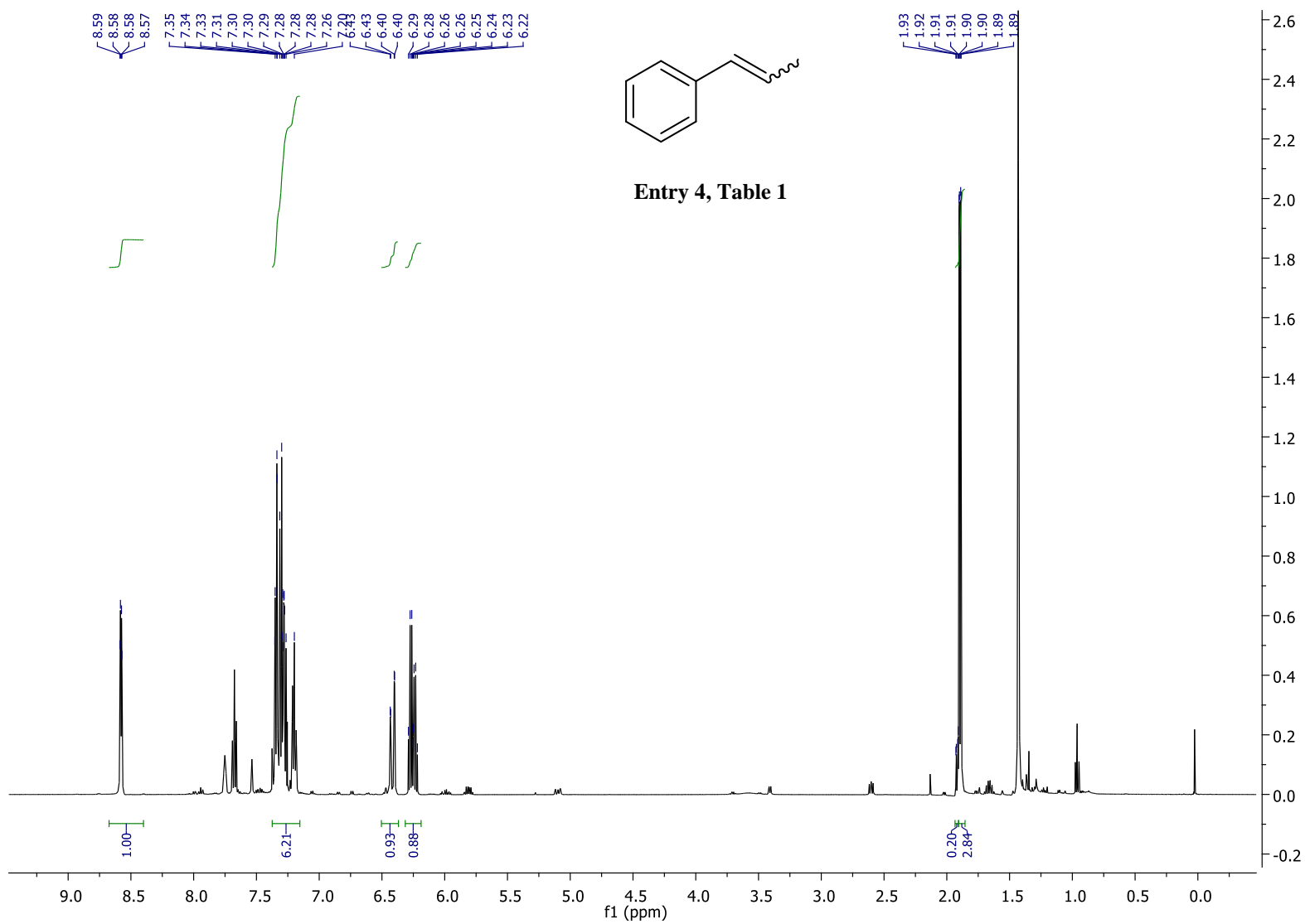


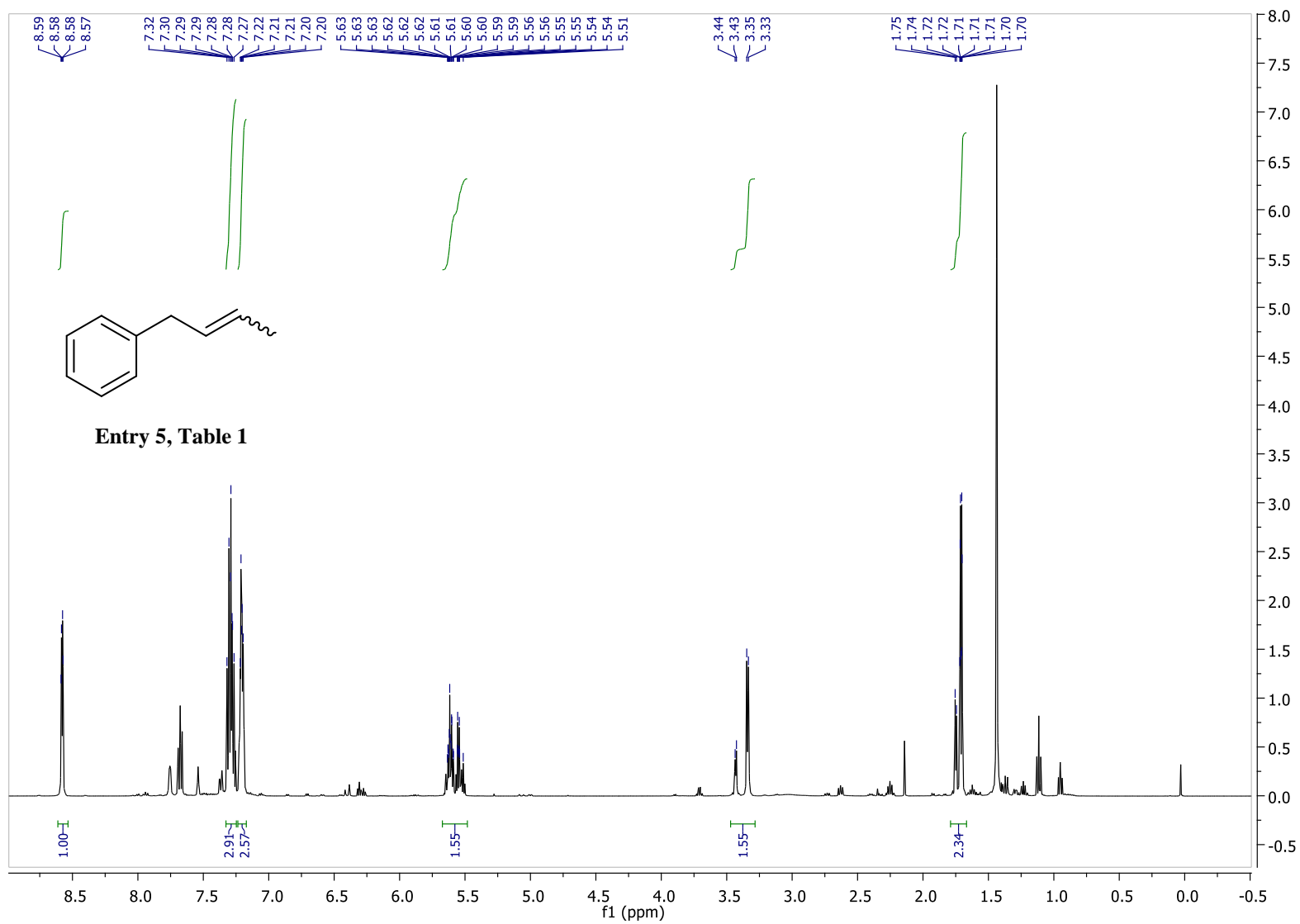


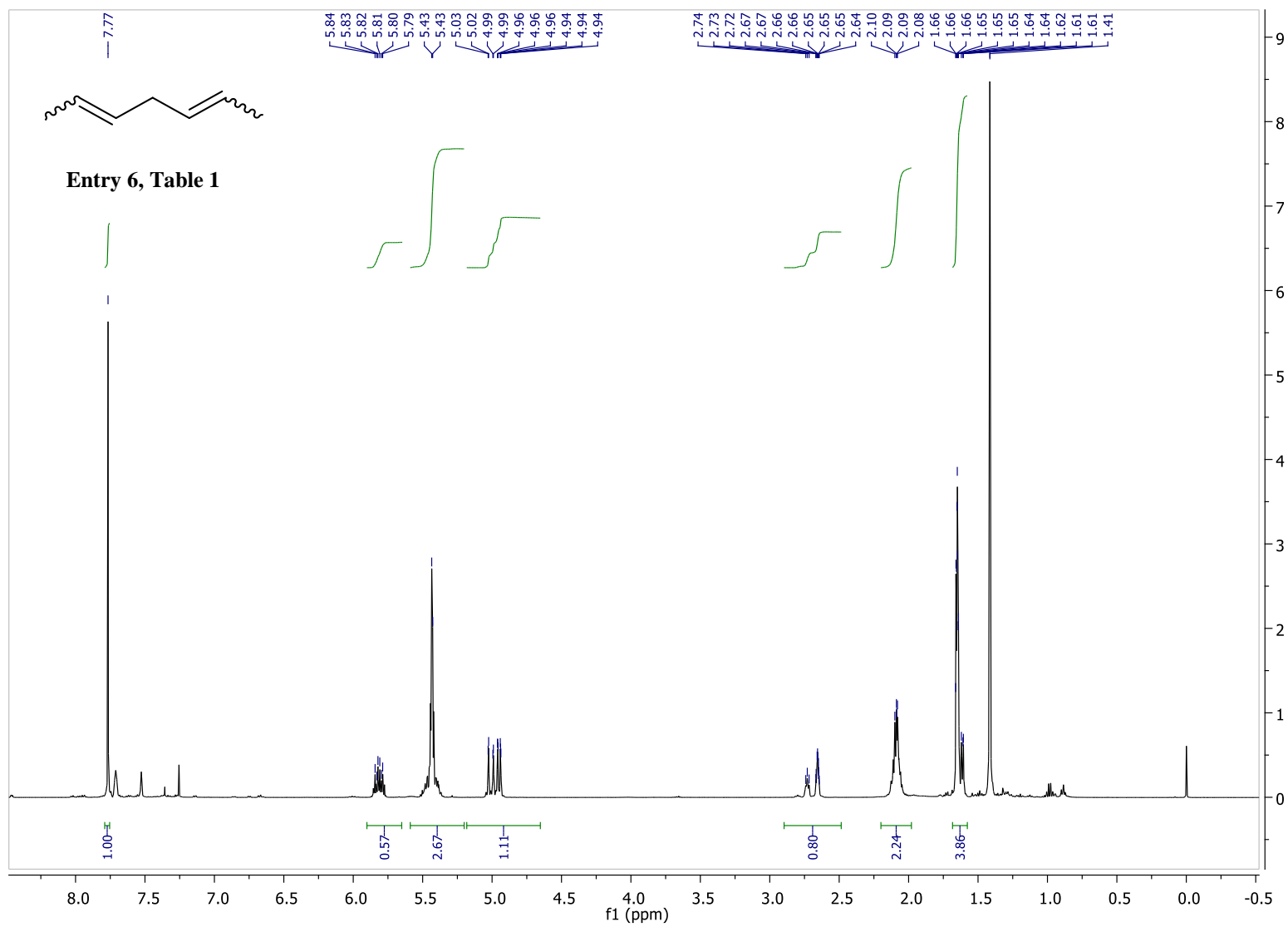


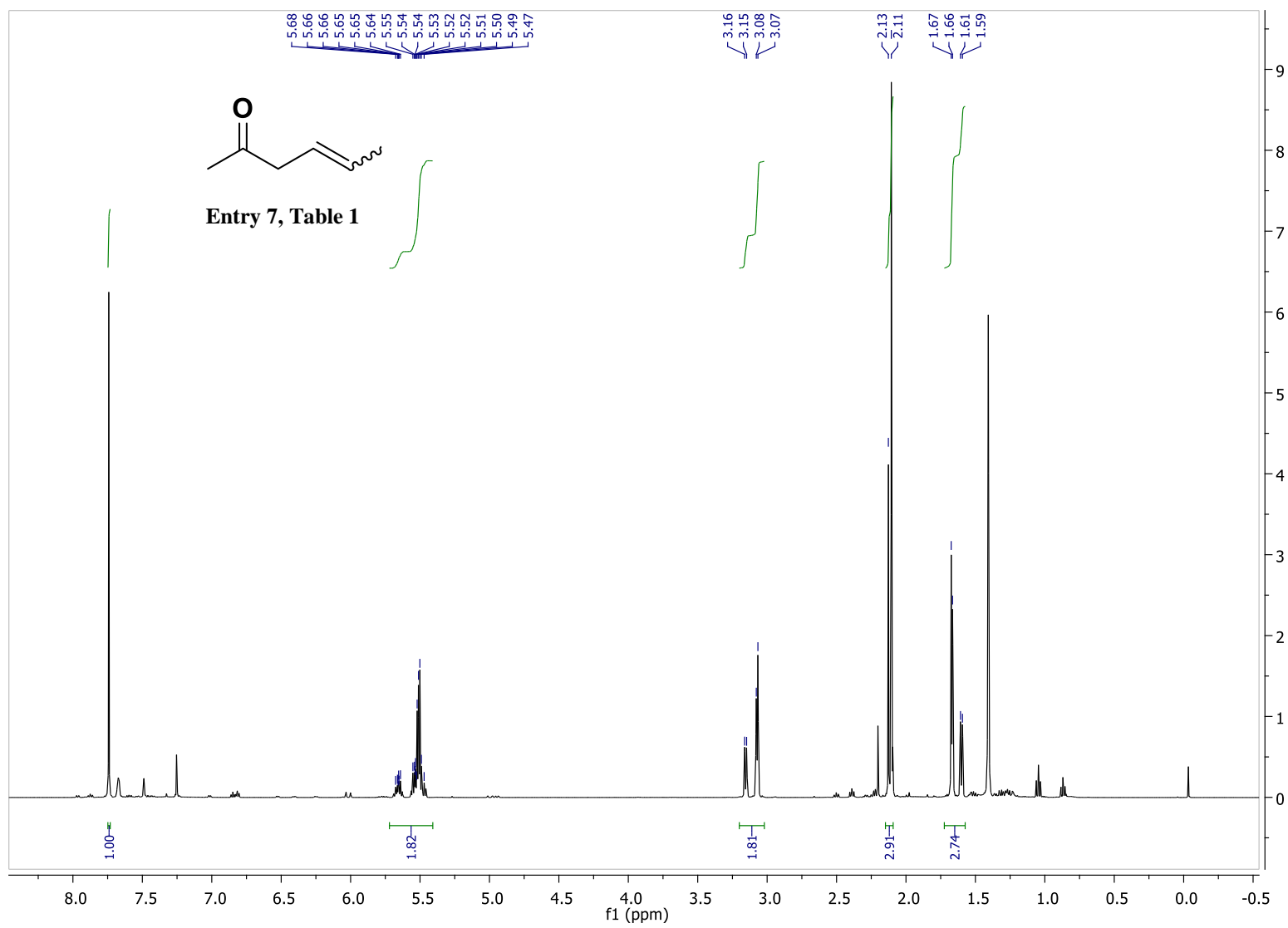


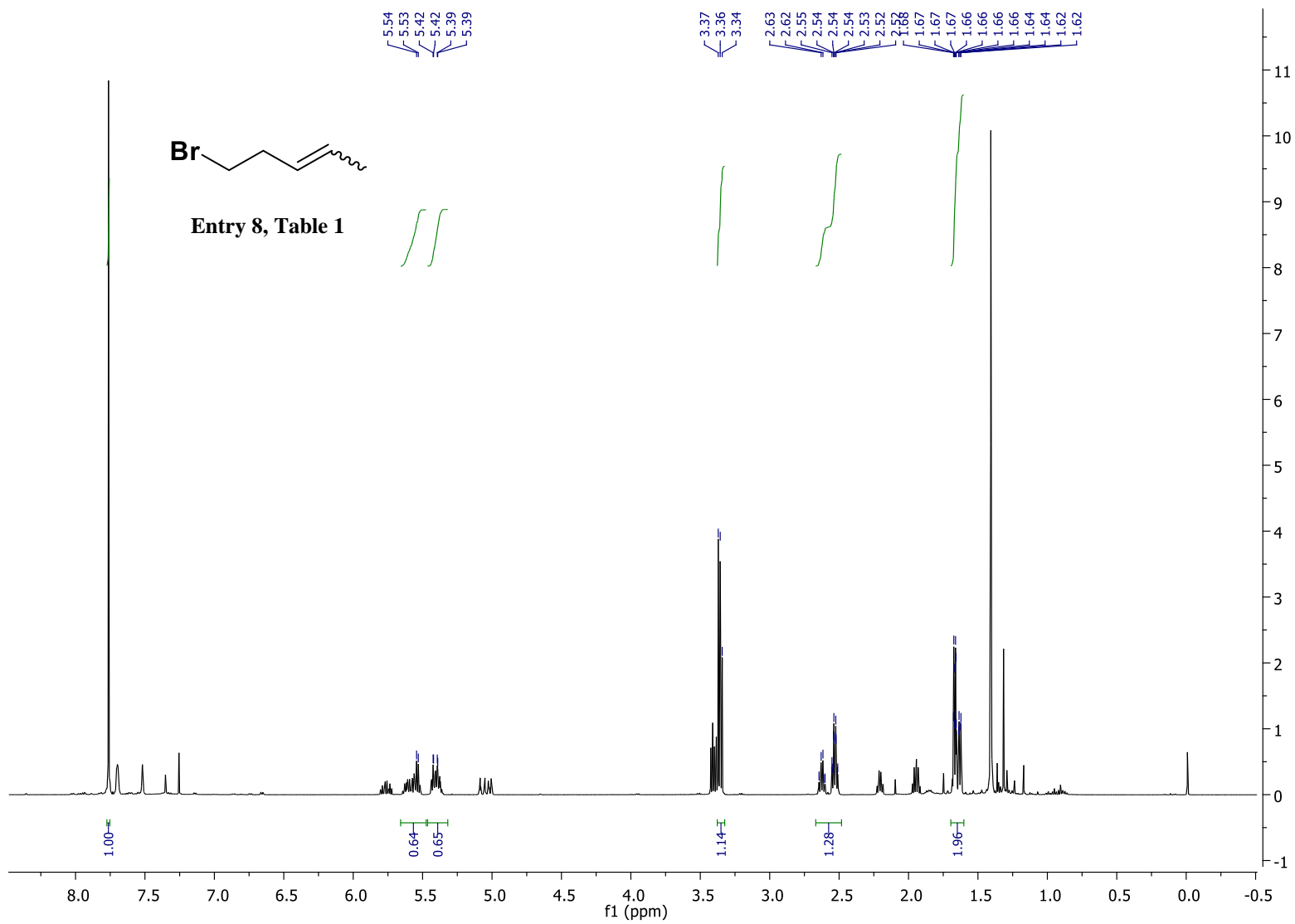


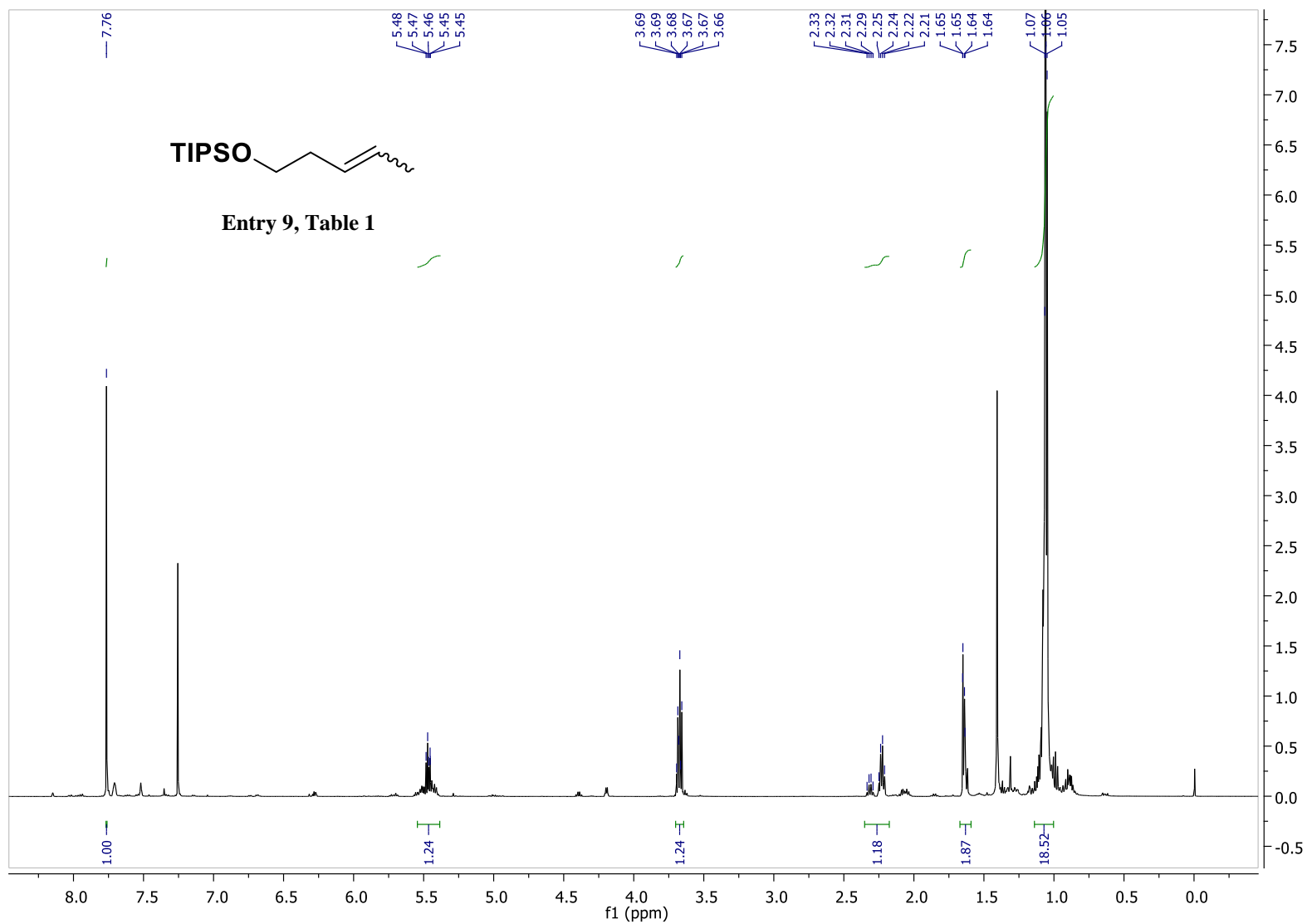


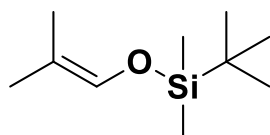












Entry 10, Table 1

