Supporting Information

Investigating the Ring-Opening Polymerization Activity of Niobium and Tantalum Ethoxides Supported by Phenoxyimine Ligands
Alyson S. Plaman and Christopher B. Durr*

Department of Chemistry, Amherst College, 25 East Drive, Amherst, Massachusetts 01002, United States of America

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Experimental Details

Some of the general experimental and analytical procedures in our lab have been described previously.¹

All metal complexes were synthesized and manipulated under a nitrogen atmosphere in an MBraun glovebox. Reagents were obtained from Sigma-Aldrich, TCI America, Strem or Alfa-Aesar and used as received unless otherwise described. rac-lactide was donated from Corbion, stored at -35 °C in a nitrogen glovebox and used as received. ε-Caprolactone was purchased from TCI America, degassed under high-vacuum, dried over 4 Å activated molecular sieves and stored sealed under nitrogen. Anhydrous solvents were purchased from Beantown Chemical and Alfa-Aesar and used as received. Deuterated solvents were purchased from Sigma-Aldrich and Cambridge Isotope Laboratory, degassed under high-vacuum, and stored in the glovebox over 4 Å activated molecular sieves.

NMR spectra were recorded using a Bruker Ascend 400 spectrometer. Elemental analysis was performed by Robertson Microlit Laboratories. Some values deviate from the theoretical, likely due to the air sensitive nature of the molecules, but are reported here regardless to demonstrate the best values found to date.

GPC analysis was performed using an Agilent PL 1260 Infinity II instrument and calibrated according to poly(styrene) standards. Crude polymer samples were dissolved overnight in HPLC grade tetrahydrofuran (THF) (2 mL) and filtered using 0.45 µm nylon filters. Samples were separated by two PLgel 5 µm Mixed-C columns connected in parallel with a solvent (THF) flow rate of 1 mL / min at 35 °C. Detection was performed with a refractive index detector. Correction factors of 0.58 for PLA and 0.56 for PCL were applied to the Mn values of all homopolymers.² No correction factor was used for the Mn determination of the copolymer sample.

Samples for single crystal X-ray diffraction (SCXRD) were isolated in the glovebox and immersed in fluorinated oil. Each crystal was mounted on a MiTeGen MicroMount and cooled to the desired temperature with an Oxford Cryostream 800. Data was collected on a Rigaku Synergy-I diffractometer using a Cu radiation source, Kα = 1.541 Å, and equipped with a HyPix3000 detector. Data integration and absorption correction was performed with CrysAlis Pro.³ Structural solution was performed with SHELXT³ followed by data refinement with SHELXL⁵ within the OLEX2 GUI.⁶ Structural data has been deposited in the Cambridge Structural Database (CSD) and has been assigned registration numbers 2164469 – 2164480.

Catalysts 2, 5 and 3e crystallized with highly disordered solvent in the lattice. After numerous attempts to model the disorder, the solvent mask protocol of OLEX2 was utilized.⁶ Further details can be found embedded within the CIF.
Ligand Synthesis

The syntheses of HL_{1-3d} have been adapted from previous reports.\textsuperscript{7-12}

HL_{1} 3,5-Di-tert-butyl-salicylaldehyde (2.97 g, 12.70 mmol) was added to a round bottom flask. 2,6-Diisopropylaniline (2.25 g, 12.70 mmol) was added to the round bottom and ethanol (25 mL) was added to dissolve both reactants along with 2 drops of formic acid. The reaction was refluxed at 95 °C for 18 h. The round bottom was then placed in a -15 °C freezer. Light yellow sticky solid was filtered and dried via vacuum for 6 hours. The ligand was then dissolved in ethyl acetate and magnesium sulfate was added to the solution. The solution was filtered, and the dissolved product was transferred to a round bottom and placed on a rotovap for 6 hours at 80 °C to produce a light yellow glassy solid. (2.07 g, 5.26 mmol, 41%).

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{ligand1}
\caption{1H NMR assignment}
\end{figure}

\begin{table}
\centering
\begin{tabular}{c c c c}
\hline
\toprule
\textbf{1H NMR (400 MHz, CDCl\textsubscript{3}, 293 K) δ (ppm)} & \textbf{13.46 (bs, 1H, H\textsubscript{a})} & \textbf{8.31 (s, 1H, H\textsubscript{b})} & \textbf{7.53 (d, J = 2.4 Hz, 1H, H\textsubscript{c})} \\
\textbf{2.93 (hept, J = 6.9 Hz, 2H, H\textsubscript{d})} & \textbf{1.52 (s, 9H, H\textsubscript{e})} & \textbf{1.36 (s, 9H, H\textsubscript{f})} & \textbf{1.21 (d, J = 6.8 Hz, 12H, H\textsubscript{g})} \\
\bottomrule
\end{tabular}
\caption{1H NMR assignment}
\end{table}

HL_{2} 3,5-Dichlorosalicylaldehyde (2.73 g, 14.27 mmol) was added to a round bottom flask. 2,6-Diisopropylaniline (2.53 g, 14.27 mmol) was added to the round bottom and ethanol (15 mL) was added to dissolve both reactants. The solution quickly became bright orange and a precipitate formed. The reaction was refluxed at 80 °C for 4 h and subsequently placed in a -15 °C freezer. The precipitate was isolated via vacuum filtration to yield an orange powder (4.367 g, 12.47 mmol, 87%).

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{ligand2}
\caption{1H NMR assignment}
\end{figure}

\begin{table}
\centering
\begin{tabular}{c c c c}
\hline
\toprule
\textbf{1H NMR (400 MHz, CDCl\textsubscript{3}, 293 K) δ (ppm)} & \textbf{13.97 (bs, 1H, H\textsubscript{a})} & \textbf{8.24 (s, 1H, H\textsubscript{b})} & \textbf{7.51 (d, J = 2.5 Hz, 1H, H\textsubscript{c})} \\
\textbf{7.27 (d, J = 2.5 Hz, 1H, H\textsubscript{d})} & \textbf{7.21 (t, J = 2.2 Hz, 3H, H\textsubscript{e})} & \textbf{7.21 (t, J = 2.2 Hz, 3H, H\textsubscript{f})} & \textbf{7.21 (t, J = 2.2 Hz, 3H, H\textsubscript{g})} \\
\bottomrule
\end{tabular}
\caption{1H NMR assignment}
\end{table}
**HL₃α-o-Vanillin (3.267 g, 21.47 mmol)** was added to a round bottom flask and dissolved in ethanol (10mL). Aniline (2.00 g, 21.47 mmol) was added to the round bottom and bright red solution was stirred overnight. The round bottom was placed on a rotovap to remove solvent, yielding an orange solid (4.510 g, 19.85 mmol, 92%).

\[ \text{HL₃α-o-Vanillin} \]

1H NMR assignment

1H NMR (400 MHz, CDCl₃, 293 K) δ (ppm): 13.70 (bs, 1H, Hₐ), 8.63 (s, 1H, Hₐ), 7.43 (m, 2H, Hₐ), 7.29 (m, 3H, Hₐ), 7.03 (dd, J = 7.7, 1.5 Hz, 1H, Hₐ), 7.01 (dd, J = 8.0, 1.5 Hz, 1H, Hₐ), 6.88 (t, J = 7.9 Hz, 1H, Hₐ), 3.94 (s, 3H, Hₐ).

**HL₃b-o-Vanillin (1.00 g, 6.57 mmol)** was added to a round bottom flask and dissolved in ethanol (10mL). 2,6-Dimethylaniline (0.796, 6.57 mmol) and formic acid (5 drops) were added to the round bottom to give an orange solution. Reaction was refluxed at 80 °C for 6 hours and then filtered and dried via vacuum filtration to give a yellow powder (1.50 g, 5.87 mmol, 89%).

\[ \text{HL₃b-o-Vanillin} \]

1H NMR assignment

1H NMR (400 MHz, CDCl₃, 293 K) δ (ppm): 13.53 (bs, 1H, Hₐ), 8.35 (s, 1H, Hₐ), 7.10 (d, J = 7.2 Hz, 2H, Hₐ), 7.03 (m, 1H, Hₐ), 6.97 (dd, J = 7.8, 1.6 Hz, 1H, Hₐ), 6.91 (t, J = 7.8 Hz, 1H, Hₐ), 3.96 (s, 3H, Hₐ), 2.21 (s, 6H, Hₐ).

**HL₃c-o-Vanillin (5 g, 32.86 mmol)** was added to a round bottom flask and dissolved in ethanol (30mL). 2,6-Diisopropylaniline (5.83 g, 32.86 mmol) and several drops of formic acid were added to the stirring o-vanillin, producing an orange solution. The reaction was refluxed at 80 °C for 18 hours and the resulting yellow powder was filtered and dried via vacuum filtration (5.0 g, 16.1 mmol, 82%).

\[ \text{HL₃c-o-Vanillin} \]
\[ ^1H \text{ NMR assignment} \]

\[ ^1H \text{ NMR (400 MHz, CDCl}_3, 293 \text{ K}) \delta (ppm): 13.55 (bs, 1H, H_a), 8.33 (s, 1H, H_b), 7.20 (t, J = 2.4 \text{ Hz}, 3H, H_c), 7.03 (dd, J = 7.9, 1.6 \text{ Hz}, 1H, H_d), 7.00 (dd, J = 7.9, 1.6 \text{ Hz}, 1H, H_d), 6.93 (t, J = 7.9 \text{ Hz}, 1H, H_e), 3.98 (s, 3H, H_f), 3.02 (hept, J = 6.8 \text{ Hz}, 2H, H_g), 1.19 (d, J = 6.6 \text{ Hz}, 12H, H_h). \]

\[ \text{HL}_{3d} \alpha\text{-Vanillin (1.455 g, 9.56 mmol) was added to a round bottom flask and dissolved in ethanol (10 mL). 2,4,6-Tri-\text{-} \text{tert-} \text{-} \text{butylaniline (2.50 g, 9.56 mmol) was added to the \alpha\text{-}vanillin solution and reaction was refluxed at 90}^\circ \text{C for 14 hours and then stirred at room temperature for 96 hours. Product was filtered and dried over vacuum to yield a light yellow powder (2.715 g, 6.86 mmol, 72%).} \]

\[ ^1H \text{ NMR assignment} \]

\[ ^1H \text{ NMR (400 MHz, CDCl}_3, 293 \text{ K}) \delta (ppm): 13.76 (s, 1H, H_a), 8.24 (s, 1H, H_b), 7.40 (s, 2H, H_c), 7.03 (m, 1H, H_d), 6.91 (m, 2H, H_e), 3.97 (s, 3H, H_f), 1.35 (s, 9H, H_g), 1.34 (s, 18H, H_h). \]

\[ \text{Catalyst Synthesis} \]

\[ \text{Catalyst 1} \]

\[ \text{HL}_1 (0.309 \text{ g, 0.785 mmol) and Nb(OEt)}_5 (0.250 \text{ g, 0.785 mmol) were separately dissolved in a minimum of toluene (2 and 1 mL, respectively) and mixed. The yellow reaction mixture was stirred at room temperature for 16 hours. Toluene was removed under vacuum followed by addition of pentane (2 mL). Removal of the pentane under vacuum yielded a yellow powder (0.480 g, 0.722 mmol, 92%).} \]
Removal of the pentane under vacuum yielded a minimum of toluene (0.786 mmol) and Nb(OEt)₅ (0.250 g, 0.786 mmol) were separately dissolved in a minimum of toluene (2 and 1 mL, respectively) and mixed. The yellow reaction mixture was stirred at room temperature for 16 hours. Toluene was removed under vacuum followed by addition of pentane (2 mL). Removal of the pentane under vacuum yielded a yellow powder (0.486 g, 0.781 mmol, 99%).

**Catalyst 2**

\[
\text{HL}_2 (0.275 g, 0.786 \text{ mmol}) \text{ and Nb(OEt)}_5 (0.250 g, 0.786 \text{ mmol}) \text{ were separately dissolved in a minimum of toluene (2 and 1 mL, respectively) and mixed. The yellow reaction mixture was stirred at room temperature for 16 hours. Toluene was removed under vacuum followed by addition of pentane (2 mL). Removal of the pentane under vacuum yielded a yellow powder (0.486 g, 0.781 mmol, 99%).}
\]

**Elemental Analysis:**

For Catalyst 1:
- C: 63.14%
- H: 8.78%
- N: 2.10%

Found: C, 62.07; H, 7.80; N 2.05%

For Catalyst 2:
- C: 52.10%
- H: 6.48%
- N: 2.25%

Found: C, 51.58; H, 6.27; N 2.28%
Catalyst 3a

HL\textsubscript{3a} (0.179 g, 0.786 mmol) and Nb(OEt)\textsubscript{5} (0.250, 0.786 mmol) were separately dissolved in toluene (3 and 1 mL, respectively) and mixed. The orange reaction mixture was stirred at room temperature for 16 hours. Toluene was removed under vacuum followed by the addition of pentane (6 mL). Removal of pentane under vacuum yielded an amorphous yellow solid (0.356 g, 0.713 mmol, 91%).

\begin{align*}
\text{\textsuperscript{1}H NMR assignment} & \quad \text{\textsuperscript{13}C NMR assignment} \\
\begin{array}{c}
\text{8.21 (s, 1H, H\textsubscript{a}), 7.40 (m, 2H, H\textsubscript{b}), 7.30 (m, 3H, H\textsubscript{c}), 7.06 (dd, J = 7.8, 1.6 Hz, 1H, H\textsubscript{d}), 6.95 (dd, J = 7.8, 1.6 Hz, 1H, H\textsubscript{e}), 6.71 (t, J = 7.8 Hz, 1H, H\textsubscript{f}), 4.62 (q, J = 7.0 Hz, 2H, H\textsubscript{g}), 4.12 (m, 4H, H\textsubscript{h}), 3.94 (s, 3H, H\textsubscript{i}), 3.54 (q, J = 7.0 Hz, 2H, H\textsubscript{g}), 1.10 (t, J = 7.0 Hz, 6H, H\textsubscript{i}), 0.90 (t, J = 7.0 Hz, 3H, H\textsubscript{i}). \text{\textsuperscript{13}C{}{\textsuperscript{1}H} NMR (101 MHz, CDCl\textsubscript{3})}  \\
\delta (ppm): 166.75 (C\textsubscript{5}), 155.48 (C\textsubscript{11}), 153.24 (C\textsubscript{4}), 150.42 (C\textsubscript{10}), 128.68 (C\textsubscript{3}), 126.95 (C\textsubscript{7}), 126.23 (C\textsubscript{1}), 123.39 (C\textsubscript{2}), 121.12 (C\textsubscript{8}), 119.16 (C\textsubscript{9}), 116.48 (C\textsubscript{6}), 71.70 (C\textsubscript{13}), 69.84 (C\textsubscript{13}), 67.28 (C\textsubscript{13}), 57.28 (C\textsubscript{12}), 18.71 (C\textsubscript{14}), 17.95 (C\textsubscript{14}), 17.74 (C\textsubscript{14}). \text{Elemental Analysis: C}_{22}\text{H}_{32}\text{NO}_{6}\text{Nb (499.41 g/mol) Calculated: C, 52.91; H, 6.46; N 2.80 %}. \text{Found: C, 51.38; H, 5.95; N 2.87 %}
\end{array}
\end{align*}

Catalyst 3b

HL\textsubscript{3b} (0.201 g, 0.786 mmol) and Nb(OEt)\textsubscript{5} (0.250, 0.786 mmol) were separately dissolved in toluene (3 and 1 mL, respectively) and mixed. The yellow reaction mixture was stirred at room temperature for 16 hours. Toluene was removed under vacuum followed by the addition of pentane (6mL). Removal of pentane under vacuum yielded a highly viscous yellow oil (0.350 g, 0.665 mmol, 85%).
$^1$H NMR assignment

$^1$H NMR (400 MHz, CDCl$_3$, 293 K) $\delta$ (ppm): 7.96 (s, 1H, H$_a$), 7.19 (m, 3H, H$_b$), 7.05 (m, 4H, H$_{b,c}$), 6.85 (dd, $J = 7.9$, 1.6 Hz, 1H, H$_d$), 6.67 (t, $J = 7.9$ Hz, 1H, H$_e$), 4.57 (bs, 2H, H$_f$), 4.26 (bs, 2H, H$_g$), 4.10 (bs, 2H, H$_h$), 3.94 (s, 3H, H$_i$), 3.46 (bs, 2H, H$_j$), 2.29 (s, 6H, H$_{k,l}$), 1.32 (bs, 3H, H$_m$), 1.09 (bs, 6H, H$_n$), 0.92 (bs, 3H, H$_i$). $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$) $\delta$ (ppm): 168.81 (C$_8$), 155.70 (C$_{12}$), 152.01 (C$_4$), 150.46 (C$_{11}$), 130.80 (C$_3$), 128.12 (C$_1$), 126.90 (C$_8$), 125.60 (C$_2$), 121.25 (C$_7$), 118.87 (C$_{10}$), 116.08 (C$_9$), 71.29 (C$_{14}$), 70.04 (C$_{15}$), 67.01 (C$_{16}$), 57.28 (C$_{17}$), 18.48 (C$_{18}$), 18.40 (C$_{19}$). Elemental Analysis: C$_{28}$H$_{44}$NO$_6$Nb (583.57 g/mol) Calculated: C, 56.18; H, 7.15; N 2.40 %. Found: C, 56.18; H, 7.15; N 2.34 %

Catalyst 3c

HL$_{3c}$ (0.278 g, 0.893 mmol) and Nb(OEt)$_5$ (0.284, 0.893 mmol) were separately dissolved in toluene (2 and 1 mL, respectively) and mixed. The yellow reaction mixture was stirred at room temperature for 16 hours. Toluene was removed under vacuum followed by addition of pentane (4 mL). Removal of pentane under vacuum yielded a yellow powder (0.433 g, 0.741 mmol, 83%).

$^1$H NMR assignment

$^1$H NMR (400 MHz, CDCl$_3$, 293 K) $\delta$ (ppm): 7.96 (s, 1H, H$_a$), 7.19 (m, 3H, H$_b$), 7.04 (dd, $J = 7.7$, 1.6 Hz, 1H, H$_d$), 6.83 (dd, $J = 7.8$, 1.6 Hz, 1H, H$_e$), 6.67 (t, $J = 7.8$ Hz, 1H, H$_f$), 4.55 (bs, 2H, H$_g$), 4.29 (bs, 2H, H$_h$), 4.05 (bs, 2H, H$_i$), 3.95 (s, 3H, H$_j$), 3.33 (m, 4H, H$_{k,l}$), 1.10 (m, 24H, H$_l$). $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$) $\delta$ (ppm): 168.56 (C$_8$), 155.88 (C$_{12}$), 152.17 (C$_4$), 150.44 (C$_{11}$), 130.80 (C$_3$), 128.22 (C$_1$), 126.93 (C$_8$), 125.63 (C$_2$), 121.25 (C$_7$), 118.97 (C$_{10}$), 116.08 (C$_9$), 71.29 (C$_{14}$), 70.04 (C$_{15}$), 67.01 (C$_{16}$), 57.28 (C$_{17}$), 18.48 (C$_{18}$), 18.40 (C$_{19}$). Elemental Analysis: C$_{28}$H$_{44}$NO$_6$Nb (583.57 g/mol) Calculated: C, 57.63; H, 7.60; N 2.40 %. Found: C, 56.18; H, 7.15; N 2.34 %
Catalyst 3d

HL_{3d} (0.311 g, 0.786 mmol) and Nb(OEt)$_5$ (0.250 g, 0.786 mmol) were separately dissolved in toluene (2 and 1 mL, respectively) and mixed. Reaction was stirred at room temperature for 16 hours, heated at 90 °C for 6 hours, and stirred at room temperature for an additional 16 hours. Toluene was removed under vacuum followed by the addition of pentane (10 mL). Removal of pentane yielded a yellow sticky solid (0.2080 g, 0.312 mmol, 40%).

1H NMR assignment

1H NMR (400 MHz, CDCl$_3$, 293 K) δ (ppm): 8.70 (s, 1H, H$_a$), 7.87 (dd, $J = 7.9$, 1.4 Hz, 1H, H$_b$), 7.39 (s, 2H, H$_c$), 7.01 (dd, $J = 7.9$, 1.4 Hz, 1H, H$_d$), 6.82 (t, $J = 7.9$ Hz, 1H, H$_e$), 4.31 (q, $J = 7.2$ Hz, 8H, H$_f$), 4.15 (s, 3H, H$_g$), 1.38 (s, 9H, H$_h$), 1.35 (s, 18H, H$_h$), 1.18 (t, $J = 7.1$, 12H, H$_i$). 13C($^1$H) NMR (101 MHz, CDCl$_3$) δ (ppm): 158.08 (C$_6$), 154.84 (C$_{12}$), 151.57 (C$_3$), 149.98 (C$_{11}$), 143.59 (C$_4$), 138.54 (C$_4$), 123.09 (C$_7$), 121.75 (C$_{3,10}$), 116.72 (C$_9$), 112.63 (C$_8$), 69.90 (C$_{14}$), 59.00 (C$_{13}$), 36.00 (C$_4$), 34.75 (C$_2$), 31.74 (C$_1$), 31.54 (C$_1$), 18.50 (C$_{15}$).

*Yield contains mixture of products.

Catalyst 4

HL$_2$ (0.242 g, 0.615 mmol) and Ta(OEt)$_5$ (0.250 g, 0.615 mmol) were separately dissolved in a minimum of toluene (2 and 1 mL, respectively) and mixed. The yellow reaction mixture was stirred at room temperature for 16 hours. Toluene was removed under vacuum followed by addition of pentane (2 mL). Removal of the pentane under vacuum yielded a yellow powder (0.331 g, 0.439 mmol, 71%).
Catalyst 5

HL₂ (0.369 g, 1.056 mmol) and Ta(OEt)₅ (0.429 g, 1.056 mmol) were separately dissolved in a minimum of toluene (2 and 1 mL, respectively) and mixed. The yellow reaction mixture was stirred at room temperature for 16 hours. Toluene was removed under vacuum followed by addition of pentane (6 mL). Removal of the pentane under vacuum yielded a yellow powder (0.734 g, 1.033 mmol, 98%).

\[ ^1H \text{ NMR (400 MHz, CDCl}_3, 293 K) \delta (ppm): 7.95 (s, 1H), 7.59 (d, } J = 2.6 \text{ Hz, 1H), 7.18 (m, 3H), 6.98 (d, } J = 2.6 \text{ Hz, 1H), 4.60 (q, } J = 7.0 \text{ Hz, 2H), 4.30 (dq, } J = 10.8, 7.0 \text{ Hz, 2H), 4.09 (dq, } J = 10.8, 7.0 \text{ Hz, 2H), 3.44 (m, 4H), 1.53 (s, 9H), 1.29 (s, 9H), 1.27 (m, 9H), 1.04 (m, 12H), 0.84 (t, } J = 6.9 \text{ Hz, 3H).} \]

\[ ^{13}C \text{ (} ^1H \text{) NMR (101 MHz, CDCl}_3) \delta (ppm): 170.32, 161.26, 149.44, 141.93, 138.96, 138.89, 131.10, 128.64, 126.83, 123.60, 120.83, 68.61, 67.73, 65.31, 35.26, 34.02, 31.39, 29.70, 27.19, 25.91, 23.12, 22.35, 19.39, 18.94, 18.33, 14.07. \]

Elemental Analysis: C₃₉H₄₅NOS₄Ta (753.80 g/mol) Calculated: C, 55.77%; H, 7.76%; N 1.86%. Found: C, 54.65%; H, 7.36; N 1.75%
Catalyst 6a

HL$_{3a}$ (0.139 g, 0.615 mmol) and Ta(OEt)$_5$ (0.250, 0.615 mmol) were separately dissolved in toluene (2 and 1 mL, respectively) and mixed. The orange reaction mixture was stirred at room temperature for 16 hours. Toluene was removed under vacuum followed by the addition of pentane (8 mL). Removal of pentane under vacuum yielded an amorphous yellow solid (0.305 g, 0.521 mmol, 84%).

\[ ^1H \text{ NMR assignment} \]

\[ ^{13}C \text{ NMR assignment} \]

$^1$H NMR (400 MHz, CDCl$_3$, 293 K) $\delta$ (ppm): 8.19 (s, 1H, H$_a$), 7.40 (m, 2H, H$_b$), 7.32 (m, 3H, H$_c$), 7.08 (dd, $J = 7.7$, 1.6 Hz, 1H, H$_d$), 6.96 (dd, $J = 7.9$, 1.6 Hz, 1H, H$_e$), 6.72 (t, $J = 7.8$ Hz, 1H, H$_f$), 4.71 (q, $J = 7.0$ Hz, 2H, H$_g$), 4.18 (m, 4H, H$_h$), 3.93 (s, 3H, H$_i$), 3.62 (q, $J = 7.0$ Hz, 2H, H$_j$), 1.37 (t, $J = 7.0$ Hz, 3H, H$_k$), 1.07 (t, $J = 7.0$ Hz, 6H, H$_l$), 0.87 (t, $J = 7.0$ Hz, 3H, H$_m$). $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$) $\delta$ (ppm): 167.20 (C$_5$), 154.91 (C$_{11}$), 152.78 (C$_4$), 150.70 (C$_{10}$), 128.70 (C$_3$), 126.80 (C$_7$), 126.44 (C$_1$), 123.53 (C$_2$), 121.64 (C$_6$), 119.52 (C$_9$), 116.91 (C$_8$), 69.56 (C$_{13}$), 67.79 (C$_{13}$), 65.84 (C$_{13}$), 57.28 (C$_{12}$), 19.11 (C$_{14}$), 18.37 (C$_{14}$), 18.12 (C$_{14}$). Elemental Analysis: C$_{22}$H$_{32}$NO$_6$Ta (587.45 g/mol) Calculated: C, 44.98; H, 5.49; N 2.38 %; Found: C, 44.46; H, 5.30; N 2.35 %

Catalyst 6b

HL$_{3b}$ (0.157 g, 0.250 mmol) and Ta(OEt)$_5$ (0.250 g, 0.615 mmol) were separately dissolved in toluene (3 and 1 mL, respectively) and mixed. The yellow reaction mixture was stirred at room temperature for 16 hours. Toluene was removed under vacuum followed by the addition of pentane (4 mL). Removal of pentane under vacuum yielded a highly viscous yellow oil (0.335 g, 0.544 mmol, 88%).
pentane under vacuum yielded a yellow powder. Toluene was removed under vacuum followed by addition of pentane (4 mL). Removal of pentane under vacuum yielded a yellow powder (0.678 g, 1.011 mmol, 90%).

**Catalyst 6c**

HL(0.348 g, 1.117 mmol) and Ta(OEt)₃ (0.454, 1.117 mmol) were separately dissolved in toluene (2 and 1 mL, respectively) and mixed. The yellow reaction mixture was stirred at room temperature for 16 hours. Toluene was removed under vacuum followed by addition of pentane (4 mL). Removal of pentane under vacuum yielded a yellow powder (0.678 g, 1.011 mmol, 90%).

**Catalyst 6c**

\[
\begin{align*}
\text{HL} &\quad \text{Ta(OEt)}_3 \\
\text{Catalyst 6c} &\quad \text{HL} (0.348 \text{ g}, 1.117 \text{ mmol}) \text{ and } \text{Ta(OEt)}_3 (0.454, 1.117 \text{ mmol}) \text{ were separately dissolved in toluene (2} \\
&\quad \text{and 1 mL, respectively) and mixed. The yellow reaction mixture was stirred at room } \\
&\quad \text{temperature for 16} \\
&\quad \text{hours. Toluene was removed under vacuum followed by addition of pentane (4 mL). Removal of} \\
&\quad \text{pentane under vacuum yielded a yellow powder (0.678 g, 1.011 mmol, 90%).}
\end{align*}
\]
Catalyst 6d

\( \text{HL}_{3d} \) (0.243 g, 0.615 mmol) and \( \text{Ta(OET)}_5 \) (0.250 g, 0.615 mmol) were separately dissolved in toluene (2 and 1 mL, respectively) and mixed. Reaction was stirred at room temperature for 16 hours, heated at 90 °C for 6 hours, and stirred at room temperature for an additional 16 hours. Toluene was removed under vacuum followed by the additional of pentane (8 mL). Removal of pentane yielded a yellow sticky solid. Synthesis yielded a mixture of products.
**Polymerization**

**ε-Caprolactone**

In a nitrogen glovebox, the catalyst (0.0876 mmol) was weighed into an oven dried glass vial with a stir bar. CL (1.00 g, 8.76 mmol) was likewise weighed into the glass vial containing the catalyst to produce a 100:1 monomer to catalyst molar ratio. The reaction was heated at 140 °C until stirring was impeded and conversion was over 90% as determined by comparison of the integrals assigned to CL (4.20 ppm) and PCL (4.07 ppm) in the ¹H NMR. Aliquots taken for determination of conversion by NMR were removed from the glovebox and quenched with wet CDCl₃.

Additionally, after full conversion was achieved, a small amount of the reaction was removed from the glovebox and quenched by immediate exposure to air. The aliquot was dissolved in THF overnight and filtered through a 0.45 µm nylon syringe filter for Mₙ and PDI determination by gel-permeation chromatography (GPC).

**rac-Lactide**

In a nitrogen glovebox, the desired catalyst (0.0694 mmol) was weighed into an oven dried glass vial containing a stir bar. The LA (1.00 g, 6.94 mmol) was likewise weighed into the glass vial containing the catalyst to produce a 100:1 monomer to catalyst molar ratio. The reaction was heated at 140 °C until stirring was impeded and conversion was over 90% as determined by comparison of the integrals assigned to LA (4.76 ppm) and PLA (5.18 ppm). Aliquots for NMR were removed from the glovebox and quenched with wet CDCl₃.

Additionally, after full conversion was achieved, a small amount of the reaction was removed from the glovebox and quenched by immediate exposure to air. The aliquot was dissolved in THF overnight and filtered through a 0.45 µm nylon syringe filter for Mₙ and PDI determination by gel-permeation chromatography (GPC).

**Copolymerization**

In a nitrogen glovebox, the desired catalyst (0.069 mmol) was weighted into an oven dried vial containing a stir bar. Both LA (1.00 g, 6.94 mmol) and CL (0.792 g, 6.94 mmol) were weighed into the vial containing the catalyst to produce a 100:100:1 CL:LA:catalyst molar ratio. The reaction was heated to 140 °C until stirring was impeded and conversion was over 90% as determined by comparison of the integrals assigned to CL (4.20 ppm) and PCL (4.07 ppm), and LA (4.76 ppm) and PLA (5.18 ppm). Aliquots for NMR were removed from the glovebox and quenched with wet CDCl₃.

Additionally, after full conversion was achieved, a small amount of the reaction was removed from the glovebox and quenched by immediate exposure to air. The aliquot was dissolved in THF overnight and filtered through a 0.45 µm nylon syringe filter for Mₙ and PDI determination by gel-permeation chromatography (GPC).

**Polymer Purification**

A representative sample of PCL, PLA and poly(caprolactone-co-lactide) were purified by dissolving the crude polymer in dichloromethane followed by precipitation in either petroleum ether (PCL) or cold methanol (PLA and copolymer). The resulting material was filtered and dried. This procedure was repeated once more to yield the purified polymer in each case.
Figure S1. $^1$H NMR spectrum of HL$_1$ in CDCl$_3$, 400 MHz, 293 K. *Remaining 3,5-Di-tert-butylsalicylaldehyde starting material.

Figure S2. $^1$H NMR spectrum of HL$_2$ in CDCl$_3$, 400 MHz, 293 K.
Figure S3. $^1$H NMR spectrum of HL$_{3a}$ in CDCl$_3$, 400 MHz, 293 K.

Figure S4. $^1$H NMR spectrum of HL$_{3b}$ in CDCl$_3$, 400 MHz, 293 K.
Figure S5. $^1$H NMR spectrum of HL$_{3c}$ in CDCl$_3$, 400 MHz, 293 K.

Figure S6. $^1$H NMR spectrum of HL$_{3d}$ in CDCl$_3$, 400 MHz, 293 K.
Figure S7. $^1$H NMR spectrum of 1 in CDCl$_3$, 400 MHz, 293 K.

Figure S8. COSY $^1$H NMR spectrum of 1 in CDCl$_3$, 293 K.
Figure S9. $^{13}$C($^1$H) NMR spectrum of 1 in CDCl$_3$, 101 MHz, 293 K.

Figure S10. HSQC spectrum of 1 in CDCl$_3$, 293 K.
Figure S11. HMBC spectrum of 1 in CDCl$_3$, 293 K.
Figure S12. $^1$H NMR spectrum of 2 in CDCl$_3$, 400 MHz, 293 K.

Figure S13. $^1$H NMR spectrum of 2 in CDCl$_3$, 400 MHz, 223 K.
Figure S14. COSY $^1$H NMR spectrum of 2 in CDCl$_3$, 293 K.

Figure S15. $^{13}$C($^1$H) NMR spectrum of 2 in CDCl$_3$, 101 MHz, 293 K.
Figure S16. HSQC spectrum of 2 in CDCl₃, 293 K.

Figure S17. HMBC spectrum of 2 in CDCl₃, 293 K.
Figure S18. $^1$H NMR spectrum of 3a in CDCl$_3$, 400 MHz, 293 K.

Figure S19. COSY $^1$H NMR spectrum of 3a in CDCl$_3$, 293 K.
Figure S20. $^{13}$C(¹H) NMR spectrum of 3a in CDCl$_3$, 101 MHz, 293 K.

Figure S21. HSQC spectrum of 3a in CDCl$_3$, 293 K.
Figure S22. HMBC spectrum of 3a in CDCl₃, 293 K.
Figure S23. $^1$H NMR spectrum of 3b in CDCl$_3$, 400 MHz, 293 K.

Figure S24. $^1$H NMR spectrum of 3b in CDCl$_3$, 400 MHz, 223 K.
Figure S25. COSY $^1$H NMR spectrum of 3b in CDCl$_3$, 293 K.

Figure S26. $^{13}$C{$^1$H} NMR spectrum of 3b in CDCl$_3$, 101 MHz, 293 K.
Figure S27. HSQC spectrum of 3b in CDCl₃, 293 K.

Figure S28. HMBC spectrum of 3b in CDCl₃, 293 K.
Figure S29. $^1$H NMR spectrum of 3c in CDCl$_3$, 400 MHz, 293 K.

Figure S30. $^1$H NMR spectrum of 3c in CDCl$_3$, 400 MHz, 223 K.
Figure S31. COSY $^1$H NMR spectrum of 3c in CDCl$_3$, 293 K.

Figure S32. $^{13}$C($^1$H) NMR spectrum of 3c in CDCl$_3$, 101 MHz, 293 K.
Figure S33. HSQC spectrum of 3c in CDCl₃, 293 K.

Figure S34. HMBC spectrum of 3c in CDCl₃, 293 K.
Figure S35. $^1$H NMR spectrum of 3d in CDCl$_3$, 400 MHz, 293 K.

Figure S36. COSY $^1$H NMR spectrum of 3d in CDCl$_3$, 293 K.
Figure S37. $^{13}$C($^1$H) NMR spectrum of 3d in CDCl$_3$, 101 MHz, 293 K.

Figure S38. HSQC spectrum of 3d in CDCl$_3$, 293 K.
Figure S39. HMBC spectrum of 3d in CDCl$_3$, 293 K.
Figure S40. $^1$H NMR spectrum of 4 in CDCl$_3$, 400 MHz, 293 K.

Figure S41. COSY $^1$H NMR spectrum of 4 in CDCl$_3$, 293 K.
Figure S42. $^{13}$C($^1$H) NMR spectrum of 4 in CDCl$_3$, 101 MHz, 293 K.

Figure S43. HSQC spectrum of 4 in CDCl$_3$, 293 K.
Figure S44. HMBC spectrum of 4 in CDCl₃, 293 K.
Figure S45. $^1$H NMR spectrum of 5 in CDCl$_3$, 400 MHz, 293 K.

Figure S46. COSY $^1$H NMR spectrum of 5 in CDCl$_3$, 293 K.
Figure S47. $^{13}$C\{$^1$H} NMR spectrum of 5 in CDCl$_3$, 101 MHz, 293 K.

Figure S48. HSQC spectrum of 5 in CDCl$_3$, 293 K.
Figure S49. HMBC spectrum of 5 in CDCl$_3$, 293 K.
Figure S50. $^1$H NMR spectrum of 6a in CDCl$_3$, 400 MHz, 293 K.

Figure S51. COSY $^1$H NMR spectrum of 6a in CDCl$_3$, 293 K.
Figure S52. $^{13}$C($^1$H) NMR spectrum of 6a in CDCl$_3$, 101 MHz, 293 K.

Figure S53. HSQC spectrum of 6a in CDCl$_3$, 293 K.
Figure S54. HMBC spectrum of 6a in CDCl₃, 293 K.
Figure S55. $^1$H NMR spectrum of 6b in CDCl$_3$, 400 MHz, 293 K.

Figure S56. COSY $^1$H NMR spectrum of 6b in CDCl$_3$, 293 K.
Figure S57. $^{13}$C{H} NMR spectrum of 6b in CDCl$_3$, 101 MHz, 293 K.

Figure S58. HSQC spectrum of 6b in CDCl$_3$, 293 K.
Figure S59. HMBC spectrum of 6b in CDCl$_3$, 293 K.
Figure S60. $^1$H NMR spectrum of 6c in CDCl$_3$, 400 MHz, 293 K.

Figure S61. COSY $^1$H NMR spectrum of 6c in CDCl$_3$, 293 K.
Figure S62. $^{13}$C($^1$H) NMR spectrum of 6c in CDCl$_3$, 101 MHz, 293 K.

Figure S63. HSQC spectrum of 6c in CDCl$_3$, 293 K.
Figure S64. HMBC spectrum of 6c in CDCl$_3$, 293 K.
Figure S65. X-ray crystal structure of 1. Thermal ellipsoids drawn at 50% probability; hydrogen atoms are excluded for clarity. (teal: niobium, dark gray: carbon, scarlet: oxygen, blue: nitrogen)

Figure S66. X-ray crystal structure of 2. Thermal ellipsoids drawn at 50% probability; hydrogen atoms and disorder are excluded for clarity. (teal: niobium, dark gray: carbon, scarlet: oxygen, blue: nitrogen, green: chlorine)
Figure S67. X-ray crystal structure of 3a. Thermal ellipsoids drawn at 50% probability; hydrogen atoms and disorder are excluded for clarity. (teal: niobium, dark gray: carbon, scarlet: oxygen, blue: nitrogen)

Figure S68. X-ray crystal structure of 3b. Thermal ellipsoids drawn at 50% probability; hydrogen atoms are excluded for clarity. (teal: niobium, dark gray: carbon, scarlet: oxygen, blue: nitrogen)
Figure S69. X-ray crystal structure of 3c. Thermal ellipsoids drawn at 50% probability; one of three molecules in the asymmetric unit shown; hydrogen atoms are excluded for clarity (teal: niobium, dark gray: carbon, scarlet: oxygen, blue: nitrogen)

Figure S70. X-ray crystal structure of 3e. Thermal ellipsoids drawn at 50% probability; disorder, solvent, and hydrogen atoms are excluded for clarity (teal: niobium, dark gray: carbon, scarlet: oxygen, blue: nitrogen)
Figure S71. X-ray crystal structure of 3f. Thermal ellipsoids drawn at 50% probability; hydrogen atoms are excluded for clarity (teal: niobium, dark gray: carbon, scarlet: oxygen, blue: nitrogen)

Figure S72. X-ray crystal structure of 4. Thermal ellipsoids drawn at 50% probability; hydrogen atoms are excluded for clarity. (light blue: tantalum, dark gray: carbon, scarlet: oxygen, blue: nitrogen)
Figure S73. X-ray crystal structure of 5. Thermal ellipsoids drawn at 50% probability; hydrogen atoms and disorder are excluded for clarity. (light blue: tantalum, dark gray: carbon, scarlet: oxygen, blue: nitrogen, green: chlorine)

Figure S74. X-ray crystal structure of 6a. Thermal ellipsoids drawn at 50% probability; one of three molecules in the asymmetric unit shown; hydrogen atoms are excluded for clarity (light blue: tantalum, dark gray: carbon, scarlet: oxygen, blue: nitrogen)
Figure S75. X-ray crystal structure of 6b. Thermal ellipsoids drawn at 50% probability; hydrogen atoms are excluded for clarity (light blue: tantalum, dark gray: carbon, scarlet: oxygen, blue: nitrogen)

Figure S76. X-ray crystal structure of 6c. Thermal ellipsoids drawn at 50% probability; one of three molecules in the asymmetric unit shown; hydrogen atoms are excluded for clarity (light blue: tantalum, dark gray: carbon, scarlet: oxygen, blue: nitrogen)
Figure S77. Selected regions of $^1$H NMR of purified PCL in CDCl$_3$ from 2 showing ethoxide endgroups.

Figure S78. Selected regions of $^1$H NMR of purified PLA in CDCl$_3$ from 5 showing ethoxide endgroups.
Figure S79. Selected regions of $^1$H (top) and $^{13}$C($^1$H) (bottom) NMR in CDCl$_3$ for purified poly(lactide-co-caprolactone) from 5. Assignments were applied from the literature.$^{13-15}$
Table S1: Crystallographic Details

|                          | Catalyst 1          | Catalyst 2          | Catalyst 4          | Catalyst 5          |
|--------------------------|---------------------|---------------------|---------------------|---------------------|
| Chemical formula         | $\text{Cs}_3\text{H}_8\text{NNbO}_5$ | $\text{Cs}_3\text{H}_8\text{Cl}_2\text{NNbO}_5$ + Solvent | $\text{Cs}_3\text{H}_8\text{NO}_5\text{Ta}$ + Solvent | $\text{Cs}_3\text{H}_8\text{Cl}_2\text{NO}_5\text{Ta}$ + Solvent |
| $M$                      | 665.73              | 622.41              | 753.77              | 710.45              |
| Crystal system, space group | Monoclinic, $P2_1/n$ | Monoclinic, $P2_1/c$ | Monoclinic, $P2_1/n$ | Monoclinic, $P2_1/c$ |
| Temperature (K)          | 100                 | 100                 | 100                 | 100                 |
| $a$ (Å)                  | 17.4925 (1)         | 12.2594 (1)         | 17.5042 (2)         | 12.3041 (2)         |
| $b$ (Å)                  | 9.7098 (1)          | 14.9618 (1)         | 9.7162 (1)          | 14.8403 (2)         |
| $c$ (Å)                  | 21.0656 (1)         | 17.2931 (2)         | 21.0597 (2)         | 17.2175 (2)         |
| $\alpha$ ($^\circ$)     | 90                  | 90                  | 90                  | 90                  |
| $\beta$ ($^\circ$)      | 96.823 (1)          | 93.696 (1)          | 96.761 (1)          | 93.448 (1)          |
| $\gamma$ ($^\circ$)     | 90                  | 93.696 (1)          | 96.761 (1)          | 93.448 (1)          |
| $V$ (Å$^3$)              | 3552.62 (5)         | 3165.35 (5)         | 3556.81 (6)         | 3138.17 (8)         |
| $Z$                      | 4                   | 4                   | 4                   | 4                   |
| Radiation type           | Cu Ka               | Cu Ka               | Cu Ka               | Cu Ka               |
| $\mu$ (mm$^{-1}$)        | 3.06                | 4.92                | 6.00                | 8.30                |
| Crystal size (mm)        | 0.23 x 0.12 x 0.10  | 0.15 x 0.07 x 0.05  | 0.25 x 0.06 x 0.04  | 0.18 x 0.09 x 0.06  |
| Diffractometer           | XtaLAB Synergy, Single source at home/near, HyPix3000 | XtaLAB Synergy, Single source at home/near, HyPix3000 | XtaLAB Synergy, Single source at home/near, HyPix3000 | XtaLAB Synergy, Single source at home/near, HyPix3000 |
| Absorption correction$^3$| Multi-scan CrysAlis PRO 1.171.41.110a | Multi-scan CrysAlis PRO 1.171.41.117a | Multi-scan CrysAlis PRO 1.171.41.110a | Multi-scan CrysAlis PRO 1.171.41.117a |
| $T_{\text{min}}, T_{\text{max}}$ | 0.887, 1.000       | 0.760, 1.000        | 0.615, 1.000        | 0.466, 1.000        |
| No. of measured, independent and observed [$I > 2s(I)$] reflections | 66918, 6497, 6155 | 41357, 5802, 5186 | 35399, 6458, 5874 | 31224, 5745, 4876 |
| $R_{\text{int}}$        | 0.044               | 0.042               | 0.040               | 0.060               |
| (sin $\theta$/$\lambda$)$_{\text{max}}$ (Å$^{-1}$) | 0.603               | 0.603               | 0.603               | 0.604               |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.022, 0.055, 1.05  | 0.028, 0.071, 1.06  | 0.021, 0.049, 1.03  | 0.061, 0.158, 1.05  |
| No. of reflections       | 6497                | 5802                | 6458                | 5745                |
| No. of parameters        | 402                 | 361                 | 396                 | 356                 |
| No. of constraints       | 0                   | 27                  | 0                   | 0                   |
| H-atom treatment         | Mixed               | Mixed               | Mixed               | Mixed               |
| $\Delta \rho_{\text{max}}, \Delta \rho_{\text{min}}$ (e Å$^{-3}$) | 0.31, -0.40         | 0.57, -0.60         | 0.52, -0.75         | 2.29, -2.73         |

Tables have been adapted with the help of IUCr’s online publishing tools.\textsuperscript{16}
Table S2: Crystallographic Details

|                          | Catalyst 3a                          | Catalyst 3b                          | Catalyst 3c                          |
|--------------------------|--------------------------------------|--------------------------------------|--------------------------------------|
| Chemical formula         | C$_{22}$H$_{32}$NNbO$_6$             | C$_{24}$H$_{36}$NNbO$_6$             | C$_{28}$H$_{44}$NNbO$_6$             |
| Mr                       | 499.39                               | 527.45                               | 583.55                               |
| Crystal system, space group | Monoclinic, Cc                      | Monoclinic, P2$_1$/c                 | Triclinic, P -1                       |
| Temperature (K)          | 100                                  | 100                                  | 100                                  |
| a (Å)                    | 15.7243 (3)                          | 11.8342 (2)                          | 11.0668 (1)                          |
| b (Å)                    | 10.7481 (2)                          | 11.7617 (2)                          | 11.7096 (1)                          |
| c (Å)                    | 14.2461 (2)                          | 18.6313 (2)                          | 34.2613 (4)                          |
| α (°)                    | 90                                   | 90                                   | 88.898 (1)                           |
| β (°)                    | 100.360 (2)                          | 104.070 (1)                          | 84.237 (1)                           |
| γ (°)                    | 90                                   | 90                                   | 81.220 (1)                           |
| V (Å$^3$)                | 2368.43 (7)                          | 2515.50 (7)                          | 4365.61 (8)                          |
| Z                        | 4                                    | 4                                    | 6                                    |
| Radiation type           | Cu Ka                                | Cu Ka                                | Cu Ka                                |
| μ (mm$^{-1}$)            | 4.44                                 | 4.21                                 | 3.69                                 |
| Crystal size (mm)        | XtaLAB Synergy, Single source at home/near, HyPix3000 | XtaLAB Synergy, Single source at home/near, HyPix3000 | XtaLAB Synergy, Single source at home/near, HyPix3000 |
| Diffractometer           | Multi-scan CrysAlis PRO 1.171.41.110a | Multi-scan CrysAlis PRO 1.171.41.110a | Multi-scan CrysAlis PRO 1.171.41.110a |
| Absorption correction    | 0.17 × 0.09 × 0.05                    | 0.18 × 0.11 × 0.05                    | 0.13 × 0.08 × 0.04                    |
| Tmin, Tmax               | 0.681, 1.000                          | 0.643, 1.000                          | 0.919, 1.000                          |
| No. of measured, independent and observed [I > 2s(I)] reflections | 21691, 4223, 4032                     | 24652, 4564, 4184                     | 85056, 15957, 14360                   |
| $R$$_{int}$              | 0.052                                | 0.060                                | 0.037                                |
| (sin θ/λ)$_{max}$ (Å$^{-1}$) | 0.603                           | 0.601                                | 0.603                                |
| $R_1(F^2 > 2s(F^2))$, wR(F$^2$), S | 0.038, 0.099, 1.12                | 0.044, 0.121, 1.03                    | 0.026, 0.066, 1.03                    |
| No. of reflections       | 4223                                 | 4564                                 | 15957                                |
| No. of parameters        | 296                                  | 296                                  | 1008                                 |
| No. of constraints       | 2                                    | 0                                    | 0                                    |
| H-atom treatment         | Constrained                          | Constrained                          | Mixed                                |
| Δρ$_{max}$, Δρ$_{min}$ (e Å$^{-3}$) | 0.65, -1.14                     | 1.61, -1.68                          | 0.62, -0.64                          |
| Absolute Structure Parameter$^{17}$ | 0.025 (13)                   | –                                    | –                                    |

Tables have been adapted with the help of IUCr’s online publishing tools.$^{16}$
Table S3: Crystallographic Details

|                          | Catalyst 3e                                                                 | Catalyst 3f                                                                 |
|--------------------------|------------------------------------------------------------------------------|------------------------------------------------------------------------------|
| Chemical formula         | C₇₂H₁₂₂N₂Nb₄O₁₈+Solvent                                                      | C₅₆H₇₆N₂NbO₇                                                              |
| $M_r$                    | 1747.45                                                                      | 1017.20                                                                     |
| Crystal system, space group | Triclinic, $P$-1                                                              | Monoclinic, $P2_1/c$                                                       |
| Temperature (K)          | 180                                                                          | 100                                                                         |
| $a$ (Å)                  | 15.2300 (2)                                                                  | 16.6408 (3)                                                                |
| $b$ (Å)                  | 16.4422 (3)                                                                  | 10.4805 (3)                                                                |
| $c$ (Å)                  | 19.3798 (3)                                                                  | 32.5152 (10)                                                               |
| $\alpha$ (*)            | 77.469 (1)                                                                   | 90                                                                          |
| $\beta$ (*)             | 82.818 (1)                                                                   | 92.702 (2)                                                                 |
| $\gamma$ (*)            | 88.762 (1)                                                                   | 90                                                                          |
| $V$ (Å³)                | 4700.14 (13)                                                                 | 5664.5 (3)                                                                 |
| $Z$                      | 2                                                                            | 4                                                                           |
| Radiation type           | Cu $K\alpha$                                                                 | Cu $K\alpha$                                                              |
| $\mu$ (mm⁻¹)            | 4.35                                                                         | 2.12                                                                        |
| Crystal size (mm)        | $0.35 \times 0.22 \times 0.13$                                              | $0.2 \times 0.1 \times 0.04$                                              |
| Diffractometer           | XtaLAB Synergy, Single source at home/near, HyPix3000                        | XtaLAB Synergy, Single source at home/near, HyPix3000                      |
| Absorption correction²  | Multi-scan CrysAlis PRO 1.171.41.110a                                       | Multi-scan CrysAlis PRO 1.171.41.110a                                      |
| $T_{min}, T_{max}$       | 0.643, 1.000                                                                 | 0.497, 1.000                                                               |
| No. of measured, independent and observed [$I > 2s(I)$] reflections | 89541, 17036, 14475                                                           | 25966, 10118, 8322                                                         |
| $R_{int}$               | 0.065                                                                        | 0.058                                                                       |
| $(\sin \theta/\lambda)_{max}$ (Å⁻¹) | 0.604                                                                      | 0.602                                                                       |
| $R(F^2 > 2s(F^2))$, $wR(F^2)$, $S$ | 0.050, 0.145, 1.04                                                        | 0.093, 0.232, 1.09                                                         |
| No. of reflections       | 17036                                                                        | 10118                                                                       |
| No. of parameters        | 980                                                                          | 636                                                                         |
| No. of constraints       | 54                                                                           | 0                                                                           |
| H-atom treatment         | Constrained                                                                  | Constrained                                                                |
| $\Delta \rho_{max}$, $\Delta \rho_{min}$ (e Å⁻³) | 1.65, -1.18                                                                 | 4.16, -1.81                                                                |

Tables have been adapted with the help of IUCr’s online publishing tools.¹⁶
Table S4: Crystallographic Details

|                              | Catalyst 6a                              | Catalyst 6b                              | Catalyst 6c                              |
|------------------------------|------------------------------------------|------------------------------------------|------------------------------------------|
| Chemical formula             | $\text{C}_2\text{H}_32\text{NO}_6\text{Ta}$ | $\text{C}_2\text{H}_32\text{NO}_6\text{Ta}$ | $\text{C}_2\text{H}_32\text{NO}_6\text{Ta}$ |
| $M$                          | 587.43                                   | 615.49                                   | 671.59                                   |
| Crystal system, space group  | Monoclinic, $P2_1$                       | Monoclinic, $P2_1/c$                     | Triclinic, $P-1$                         |
| Temperature (K)              | 100                                       | 100                                       | 100                                       |
| $a$ (Å)                      | 8.9712 (2)                               | 11.8727 (3)                              | 11.07947 (6)                             |
| $b$ (Å)                      | 14.5233 (3)                              | 11.7358 (3)                              | 11.71800 (5)                             |
| $c$ (Å)                      | 9.0007 (2)                               | 18.6058 (4)                              | 34.21945 (16)                            |
| $\alpha$ (°)                | 90                                        | 90                                        | 88.9319 (4)                              |
| $\beta$ (°)                 | 100.390 (2)                              | 103.756 (2)                              | 84.2143 (4)                              |
| $\gamma$ (°)                | 90                                        | 90                                        | 81.2415 (4)                              |
| $V$ (Å$^3$)                  | 1153.48 (4)                              | 2518.09 (11)                             | 4368.49 (4)                              |
| $Z$                          | 2                                         | 4                                         | 6                                         |
| Radiation type               | Cu Ka                                     | Cu Ka                                     | Cu Ka                                     |
| $\mu$ (mm$^{-1}$)            | 9.10                                      | 8.37                                      | 7.29                                      |
| Crystal size (mm)            | $0.17 \times 0.11 \times 0.06$           | $0.18 \times 0.08 \times 0.06$          | $0.15 \times 0.13 \times 0.04$          |
| Diffractometer               | XtaLAB Synergy, Single source at home/near, HyPix3000 | XtaLAB Synergy, Single source at home/near, HyPix3000 | XtaLAB Synergy, Single source at home/near, HyPix3000 |
| Absorption correction$^3$   | Multi-scan CrysAlis PRO 1.171.41.117a     | Multi-scan CrysAlis PRO 1.171.41.110a     | Multi-scan CrysAlis PRO 1.171.41.110a     |
| $T_{\text{min}}, T_{\text{max}}$ | 0.505, 1.000                             | 0.400, 1.000                             | 0.743, 1.000                             |
| No. of measured, independent and observed $|I > 2\sigma(I)|$ reflections | 22030, 4203, 4091                          | 23914, 4541, 3969                         | 87499, 15945, 14806 |
| $R_{\text{int}}$             | 0.053                                     | 0.052                                     | 0.040                                     |
| $(\sin \theta/\lambda)_{\text{max}}$ (Å$^{-1}$) | 0.603                                   | 0.604                                     | 0.603                                     |
| $R[|F|^2 > 2\sigma(F)|], wR|F|^2$, $S$ | 0.032, 0.083, 1.05                        | 0.032, 0.079, 1.11                        | 0.022, 0.052, 1.03 |
| No. of reflections           | 4203                                      | 4541                                      | 15945                                     |
| No. of parameters            | 277                                       | 296                                       | 1000                                      |
| No. of constraints           | 1                                         | 0                                         | 0                                         |
| H-atom treatment             | Constrained                               | Constrained                               | Constrained                               |
| $\Delta \rho_{\text{max}}, \Delta \rho_{\text{min}}$ (e Å$^{-3}$) | 2.76, -0.84                             | 1.22, -1.02                             | 0.81, -0.77                             |
| Absolute Structure Parameter$^{17}$ | 0.163 (18)                             | –                                        | –                                         |

Tables have been adapted with the help of IUCr’s online publishing tools.$^{16}$
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