Supporting Information

Z-Selective Ethenolysis With a Ruthenium Metathesis Catalyst:

Experiment and Theory

Hiroshi Miyazaki,†§ Myles B. Herbert,†§ Peng Liu,‡ Xiaofei Dong,‡ Xiufang Xu,‡,# Benjamin K. Keitz,† Thay Ung,§ Garik Mkrtumyan,§ K. N. Houk,*,‡ and Robert H. Grubbs*,†
† Arnold and Mabel Beckman Laboratory of Chemical Synthesis, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, United States
‡ Department of Chemistry and Biochemistry, University of California, Los Angeles, 90095-1569, United States.
# Department of Chemistry, Nankai University, Tianjin 300071, P. R. China
ξ Materia Inc., 60 N. San Gabriel Blvd., Pasadena, CA, 91107, United States

Table of Contents

General Information.................................................................................................................................S3
Synthesis of 12 ...........................................................................................................................................S3
Synthesis of 15 ...........................................................................................................................................S4
Synthesis of S5..........................................................................................................................................S4
Alternative synthesis of 15 ........................................................................................................................S4
Synthesis of 16 ...........................................................................................................................................S5
Synthesis of S7..........................................................................................................................................S5
Synthesis of S8..........................................................................................................................................S5
Synthesis of 17 ...........................................................................................................................................S5
Alternative synthesis of 17 ........................................................................................................................S6
Synthesis of 18 ..........................................................................................................................................S7
Representative procedure for ethenolysis at 1 atm.................................................................S7
Representative procedure for ethenolysis at 5 atm.........................................................................S7
Formation of purely E-5-decene ........................................................................................................S7
Formation of purely E-compound 12 ...............................................................................................S8
Procedure for the ethenolysis of methyl oleate ............................................................................S8
Kinetic measurement procedure .....................................................................................................S9
GC data analysis CM.......................................................................................................................S10
Representative procedure for CM of 14 and 11 with catalyst 4...................................................S12
Representative procedure for CM of 14 and 11 with catalyst 2 ....................................................S13
Synthesis of Z-12 ............................................................................................................................S13
Representative procedure for CM of 11 and 12 without ethylene with catalyst 4.........................S13
Representative procedure for CM of 11 and 12 without ethylene with catalyst 2......................S14
Representative procedure for CM of 11 and 12 with ethylene with catalyst 4............................S14

List of Figures

Figure S1. 1H NMR (500 MHz) spectrum of 12 in CDCl3 ...............................................................S16
Figure S2. 13C NMR (126 MHz) spectrum of 12 in CDCl3 ............................................................S17
Figure S3. 1H-13C HSQC of 12 in CDCl3 .......................................................................................S18
Figure S4. 1H NMR (500 MHz) spectrum of 15 in acetone-d6 .......................................................S19
Figure S5. 13C NMR (126 MHz) spectrum of 15 in CDCl3 ............................................................S20
Figure S6. 1H-13C HSQC of 15 in CDCl3 .......................................................................................S21
Figure S7. 1H NMR (500 MHz) spectrum of S5 in CDCl3...............................................................S22
Figure S8. 13C NMR (126 MHz) spectrum of S5 in CDCl3 ............................................................S23
Figure S9. 1H NMR (500 MHz) spectrum of 16 in CDCl3 ...............................................................S24
Figure S10. 13C NMR (126 MHz) spectrum of 16 in CDCl3 ..........................................................S25
Figure S11. 1H-13C HSQC of 16 in CDCl3 .......................................................................................S26
Figure S12. 1H NMR (500 MHz) spectrum of S7 in CDCl3 .............................................................S27
Figure S13. 13C NMR (126 MHz) spectrum of S7 in CDCl3 ............................................................S28
Figure S14. 1H NMR (500 MHz) spectrum of S8 in C6D6 ...............................................................S29
Figure S15. 13C NMR (126 MHz) spectrum of S8 in CDCl3 ............................................................S30
Figure S16. 1H NMR (500 MHz) spectrum of 17 in CDCl3 .............................................................S31
Figure S17. 13C NMR (126 MHz) spectrum of 17 in CDCl3 ............................................................S32
Figure S18. 1H-13C HSQC of 17 in CDCl3 .......................................................................................S33
Figure S19. 1H NMR (500 MHz) spectrum of S8 in CDCl3 .............................................................S34
Figure S20. $^{13}$C NMR (126 MHz) spectrum of 18 in CDCl$_3$..........................................................S35
Figure S21. $^1$H-$^{13}$C HSQC of 18 in CDCl$_3$.............................................................................................................S36
Figure S22. $^1$H NMR (500 MHz) spectrum of the purely E-isomer of 11 in CDCl$_3$..........................S37
Figure S23. $^1$H NMR (500 MHz) spectrum of the purely E-isomer of 12 in CDCl$_3$..............S38

General Information
All reactions were carried out in dry glassware under an argon atmosphere using standard Schlenk technique, or in a Vacuum Atmospheres Glovebox under a nitrogen atmosphere unless otherwise specified. Commercially available reagents were used as received unless otherwise noted. Substrates for ethenolysis and olefin cross metathesis were degassed with argon prior to use. Proton peaks in the $^1$H NMR spectra corresponding to the E- and Z-isomers of all ethenolysis substrates were confirmed by HSQC analysis. THF was purified by passage through solvent purification columns and further degassed with bubbling argon.$^1$

C$_6$D$_6$ was purified by passage through a solvent purification column. CDCl$_3$ and acetone-d$_6$ were used as received. Benzylidene-bis (tricyclohexylphosphine) dichlororuthenium (S1), (1,3-Bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene) dichloro(phenylmethylene)(tricyclohexylphosphine)ruthenium (S2), and 5 were obtained from Materia, Inc. Catalyst 3 was synthesized according to a previous report.$^2$

$^1$H and $^{13}$C NMR spectra were recorded on a Varian 500 MHz spectrometer. Chemical shifts are reported in ppm downfield from Me$_4$Si by using the residual solvent peak as an internal standard. Spectra were analyzed and processed using MestReNova Ver. 7.1. High-resolution mass spectra were provided by the California Institute of Technology Mass Spectrometry Facility using JEOL JMS-600H High Resolution Mass Spectrometer. Gas chromatography data were obtained using Agilent 6850 FID gas chromatograph equipped with HP-5 (5%-phenyl)-methylpolysiloxane capillary column (Agilent).

Synthesis of 12: Representative Procedure for synthesis of E-dominant symmetric internal olefin (metathesis homocoupling of terminal olefin):

A 50 ml Schlenk flask was charged with 14 (4.2 g, 23 mmol) and S1 (190 mg, 0.23 mmol). The flask was sealed and placed on a vacuum line (Buchi Vacuum Controller B-721), and the mixture was stirred at 35 °C for 16 h under vacuum (30 mmHg). The reaction was

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quenched by adding tris(hydroxymethyl)phosphine\textsuperscript{3} (840 mg, 6.8 mmol), THF (20 ml) and water (10 ml). After stirring at 60 °C for 4 h, the mixture was extracted with diethyl ether and the organic solution was washed with water, dried over MgSO\textsubscript{4}, and concentrated \textit{in vacuo}. The resulting residue was purified by flash column chromatography (SiO\textsubscript{2}; \textit{n}-hexane ~ ethyl acetate/\textit{n}-hexane=1/20) to give pure 12 (2.6 g, 7.7 mmol, 68% yield, 78% \textit{E}) as a colorless oil. \textsuperscript{1}H NMR of \textit{E}-isomer (500 MHz, CDCl\textsubscript{3}): δ 5.41-5.37 (m, 2H), 4.04 (t, \textit{J} = 6.8 Hz, 4H), 2.04 (s, 6H), 1.98-1.94 (m, 4H), 1.66-1.55 (m, 4H), 1.43-1.19 (m, 16H). \textsuperscript{1}H NMR of \textit{Z}-isomer (500 MHz, CDCl\textsubscript{3}): δ 5.35-5.30 (m, 2H), 4.04 (t, \textit{J} = 6.8 Hz, 4H), 2.04 (s, 6H), 2.02-1.99 (m, 4H), 1.66-1.55 (m, 4H), 1.43-1.19 (m, 16H). \textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}): δ 171.3, 130.4, 64.7, 32.6, 29.6, 29.2, 29.1, 28.7, 26.0, 21.1. HRMS (EI\textsuperscript{+}): Calc for C\textsubscript{20}H\textsubscript{36}O\textsubscript{4} (M\textsuperscript{+}): 340.2614. Found: 340.2607.

\begin{center}
\begin{tikzpicture}
\node at (0,0) {\textbf{Synthesis of 15}}; \node at (0,-1.5) {
This compound was prepared from S3 (2.9 g, 29 mmol) as described in the synthesis of 12. The crude product was purified by flash column chromatography (SiO\textsubscript{2}; ethyl acetate/\textit{n}-hexane=1/1 ~ 3/1) to give pure 15 (1.7 g, 9.9 mmol, 67% yield, 68% \textit{E}) as a colorless oil. \textsuperscript{1}H NMR (500 MHz, acetone-d\textsubscript{6}): δ 5.47-5.32 (m, 2H), 3.58-3.48 (m, 4H), 3.42 (br s, 1H), 2.86-2.82 (m, 1H), 2.09-1.95 (m, 4H), 1.58-1.33 (m, 8H). \textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}): δ 130.5, 63.0, 32.4, 32.3, 25.8. HRMS (EI\textsuperscript{+}): Calc for C\textsubscript{10}H\textsubscript{20}O\textsubscript{2} (M\textsuperscript{+}): 172.1463. Found: 172.1467.
\end{tikzpicture}
\end{center}

\begin{center}
\begin{tikzpicture}
\node at (0,0) {\textbf{Synthesis of S5 and 15}}; \node at (0,-1.5) {
S5 was prepared from S4 (5.4 g, 38 mmol) as described in the synthesis of 12. The crude product was purified by flash column chromatography (SiO\textsubscript{2}; ethyl acetate/\textit{n}-hexane=1/9) to give pure S5 (4.3 g, 17 mmol, 88% yield, 81% \textit{E}) as a colorless oil. \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): δ 5.44-5.32 (m, 2H), 4.05 (t, \textit{J} = 6.7 Hz, 4H), 2.04 (s, 6H), 2.12-1.95 (m, 4H), 1.70-1.57 (m, 4H), 1.49-1.32 (m, 4H). \textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}): δ 171.4, 130.4, 64.6, 32.2, 28.2, 26.0, 21.2. HRMS (EI\textsuperscript{+}): Calc for C\textsubscript{14}H\textsubscript{25}O\textsubscript{4} ([M+H \textsuperscript{+}]): 257.1753. Found: 257.1745.
\end{tikzpicture}
\end{center}

To a solution of S5 (4.3 g, 17 mmol, 81 %E) in methanol (50 ml) was slowly added a 10 N sodium hydroxide aqueous solution (50 ml). After stirring at 60 °C for 3 h, the mixture was extracted with dichloromethane and the organic solution was washed with a saturated ammonium chloride solution, dried over MgSO₄, and concentrated *in vacuo*. The resulting residue was purified by flash column chromatography (SiO₂; ethyl acetate/n-hexane=1/1 ~ 3/1) to give pure 15 (2.5 g, 15 mmol, 87% yield, 82 %E) as a colorless oil.

**Synthesis of 16**

16 was prepared from S6 (3.3 g, 19 mmol) as described in the synthesis of 12. The crude product was purified by flash column chromatography (SiO₂; n-hexane ~ ethyl acetate/n-hexane=1/9 ~ 1/4) to give pure 16 (2.7 g, 8.6 mmol, 89% yield, 80 %E) as a colorless oil.

**Synthesis of S7, S8, and 17**

N-(Pent-4-enyl)aniline⁴ (2.2 g, 14 mmol), di-tert-butyl dicarbonate (4.5 g, 21 mmol) and 4-(dimethylamino)pyridine (170 mg, 1.4 mmol) were combined and the mixture was stirred at 90 °C for 17 h. Di-tert-butyl dicarbonate (4.5 g, 21 mmol) was added to the mixture. After addition, the mixture was stirred for an additional 5 h at 90 °C and concentrated *in vacuo*. To the resulting residue was added di-tert-butyl dicarbonate (2.5 g, 12 mmol) and the mixture was stirred overnight at 90 °C. The mixture was concentrated *in vacuo* and then the crude product was purified by flash column chromatography (SiO₂; chloroform/n-

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hexane=1/1 ~ ethyl acetate/n-hexane=1/9) to give pure S7 (1.7 g, 6.4 mmol, 47% yield, 60% E) as a red oil. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.33 (dd, $J$ = 8.3, 7.4 Hz, 2H), 7.23-7.14 (m, 3H), 5.77 (ddt, $J$ = 16.9, 10.2, 6.6 Hz, 1H), 5.03-4.88 (m, 2H), 3.68-3.58 (m, 2H), 2.09-2.00 (m, 2H), 1.64 (tt, $J$ = 9.2, 6.5 Hz, 2H), 1.42 (s, 9H). $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 154.9, 142.7, 138.0, 128.9, 127.3, 126.1, 115.1, 80.2, 49.7, 31.1, 28.5, 27.8. HRMS (FAB+): Calc for C$_{16}$H$_{23}$O$_2$N (M$^+$): 261.1729. Found: 261.1735.

S8 was prepared from S7 (8.8 g, 33 mmol) as described in the synthesis of 12. The crude product was purified by flash column chromatography (SiO$_2$; ethyl acetate/n-hexane=1/100 ~ 1/50 ~ 1/20 ~ 1/10 ~ 1/7) to give pure S8 (5.4 g, 11 mmol, 62% yield, 59% E) as a pale yellow solid. $^1$H NMR (500 MHz, C$_6$D$_6$): $\delta$ 7.14-7.06 (m, 8H), 7.01-6.93 (m, 2H), 5.35-5.18 (m, 2H), 3.73-3.54 (m, 4H), 1.97-1.81 (m, 4H), 1.59 (dq, $J$ = 9.3, 7.5 Hz, 4H), 1.40 (s, 18H). $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 154.9, 142.8, 130.0, 128.8, 127.2, 126.1, 80.1, 49.8, 29.9, 28.5, 24.6. HRMS (FAB+): Calc for C$_{30}$H$_{42}$O$_4$N$_2$ (M$^+$): 494.3145. Found: 494.3165.

To a solution of S8 (4.0 g, 8.1 mmol, 59% E) in dichloromethane (20 ml) was slowly added trifluoroacetic acid (20 ml) and the mixture was stirred for 21 h at room temperature. The reaction mixture was concentrated in vacuo, and chloroform and a saturated sodium bicarbonate solution was added to the resulting residue. The mixture was extracted with chloroform and the organic solution was dried over Na$_2$SO$_4$ and concentrated in vacuo. The resulting residue was purified by flash column chromatography (SiO$_2$; diethyl ether/n-hexane=1/4) to give pure 17 (2.3 g, 7.9 mmol, 97% yield, 60% E) as an orange oil. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.17 (ddd, $J$ = 8.6, 7.4, 1.2 Hz, 4H), 6.72-6.66 (m, 2H), 6.63-6.56 (m, 4H), 5.54-5.39 (m, 2H), 3.66 (br, 2H), 3.16-3.07 (m, 4H), 2.25-2.03 (m, 4H), 1.75-1.63 (m, 4H). $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 148.5, 130.3, 129.4, 117.3, 112.9, 43.6, 30.2, 29.4. HRMS (FAB+): Calc for C$_{20}$H$_{27}$N$_2$ ([M+H$^+$]+): 295.2174. Found: 295.2170.

**Alternative Synthesis of 17**

To a solution of S8 (1.0 g, 2.0 mmol, 59% E) in dichloromethane (5.0 ml) was added S2 (18 mg, 0.021 mmol) and the mixture was stirred for 4 h at room temperature. The reaction was quenched by adding tris(hydroxymethyl)phosphine (77 mg, 0.62 mmol), THF (20 ml) and water (20 ml). After stirring at 60 °C for 14 h, the mixture was extracted with diethyl
ether and the organic solution was washed twice with water, dried over MgSO₄, and concentrated in vacuo. The crude product S₈ (1.1 g, quant., 81 %E) was used in the next step without further purification.

17 (80 %E) was prepared from S₈ (81 %E) as described in the synthesis of 17 (60 %E).

**Synthesis of 18**

18 was prepared from S₉ (4.0 g, 41 mmol) as described in the synthesis of 12. The crude product was purified by flash column chromatography (SiO₂; ethyl acetate/n-hexane=1/3) to give pure 18 (1.2 g, 7.1 mmol, 35% yield, 72 %E) as a colorless solid. ¹H NMR (500 MHz, CDCl₃): δ 5.44-5.25 (m, 2H), 2.49-2.40 (m, 4H), 2.33-2.15 (m, 4H), 2.10 (s, 6H). ¹³C NMR (126 MHz, CDCl₃): δ 208.4, 129.5, 43.4, 30.0, 26.7. HRMS (FAB⁺): Calc for C₁₀H₁₇O₂ ([M+H⁺]: 169.1229. Found: 169.1235.

**Representative procedure for ethenolysis at 1 atm**

In a glovebox, cis-5-decene (19 μl, 0.10 mmol) and trans-5-decene (76 μl, 0.40 mmol) were combined in a 5 ml vial with a screw-cap septum top and a magnetic stir bar. A solution of the appropriate catalyst (2 or 4) was prepared in THF. THF and the desired volume of the catalyst solution were added to the 5-decene [THF total 160 μl and 4 (1.6 mg, 0.0025 mmol)]. (Before adding the catalyst, an aliquot was taken for ¹H NMR analysis to check the E/Z ratio at the starting point.) The reaction solution was sealed, removed from the glovebox, equipped with an ethylene balloon, and then purged with ethylene before heating. After the reaction solution equipped with the ethylene balloon was allowed to stir at 35 ºC for 4 h, the vial was left open to air and NMR analysis was performed.

**Representative procedure for ethenolysis at 5 atm**

**Formation of purely E 5-decene (11):** In a glovebox, cis-5-decene (88 mg, 120 μl, 0.63 mmol) and trans-5-decene (350 mg, 470 μl, 2.5 mmol) were combined in a 5 ml vial. A solution of 4 in THF was prepared, and the appropriate amount of THF and the catalyst solution were added to the 4:1 E:Z 5-decene mixture [THF total 972 μl and 4 (9.9 mg, 0.016 mmol)], and then the reaction mixture was transferred into a Fisher-Porter bottle (before adding the catalyst, an aliquot was taken for ¹H NMR analysis to check the E/Z ratio at the
starting point). The Fisher-Porter bottle was equipped with a stir bar and the top of it was equipped with a pressure gauge. The system was sealed and taken out of the glovebox to the ethylene line. The vessel was then purged with ethylene (ultra-high purity 99.95% from Matheson Tri Gas), pressurized to 5 atm, and placed in an oil bath at 35 °C. After the reaction solution was allowed to stir for 4 h, the vessel was left open to air and the reaction solution was concentrated in vacuo. The crude mixture was then dissolved in hexane and loaded onto a silica gel column for purification (100% n-hexane as the eluting solvent). Upon concentration of the fractions containing product, 5-decene was obtained as a colorless oil (310 mg, 2.2 mmol, 72% yield, >95 %E).

**Formation of purely E compound 12:**

In a glovebox, 12 (1.0 g, 3.0 mmol, 78% E) was added to a 5 ml vial. A solution of 4 in THF was prepared, and the appropriate amount of THF and the catalyst solution were added to the solution [THF total 750 μl and 4 (9.5 mg, 0.015 mmol)], and then the reaction mixture was transferred into a Fisher-Porter bottle (before adding the catalyst, an aliquot was taken for 1H NMR analysis to check the E/Z ratio at the starting point). The Fisher-Porter bottle was equipped with a stir bar and the top of it was equipped with a pressure gauge. The system was sealed and taken out of the glovebox to the ethylene line. The vessel was then purged with ethylene (ultra-high purity 99.95% from Matheson Tri Gas), pressurized to 5 atm, and placed in an oil bath at 35 °C. After the reaction solution was allowed to stir for 4 h, the vessel was left open to air and the reaction solution was concentrated in vacuo. The crude mixture was then dissolved in hexane and purified by flash column chromatography (SiO2; n-hexane ~ ethyl acetate/n-hexane=1/20). Upon concentration of the fractions containing product, 12 (790 mg, 2.3 mmol, 77% yield, >95 %E) and 14 (240 mg, 1.3 mmol, 21% yield) were obtained as colorless oils.

**Procedure for the ethenolysis of methyl oleate:**

Ethenolysis reactions were carried out using research-grade methyl oleate (>99%) that was purified by storage over activated alumina followed by filtration. The experiments were set up in a glovebox under an atmosphere of argon. Methyl oleate (10 g, 34 mmol) was charged in a Fisher-Porter bottle equipped with a stir bar, pressure gauge and dip-tube adapted to the bottle. A solution of the appropriate ruthenium catalyst (2 or 4) was prepared in dry dichloromethane, and the desired volume of this solution was added to the methyl oleate. The reaction vessel was sealed, removed from the glovebox and then attached to an ethylene line. The reaction vessel purged three times with ethylene (polymer purity 99.9%
from Matheson Tri Gas), pressurized to 150 psi, and placed in an oil bath at 40 °C. The reaction was monitored by collecting samples via the dip-tube at different routine intervals and immediately quenched by the addition of a solution of tris(hydroxymethyl)phosphine (1.0 mL, 1.0 M) in isopropanol. The samples were then heated to 60 °C for 1 hour, diluted with distilled water, extracted with hexanes, and analyzed by GC. The GC analyses were run using a flame ionization detector. Column: Rtx-5 from Restek, 30 m - 0.25 mm i.d. - 0.25 μm film thickness. GC and column conditions: injection temperature, 250 °C; detector temperature, 280 °C; oven temperature, starting temperature, 100 °C; hold time, 1 min. The ramp rate was 10 °C/min to 250 °C, hold time 12 min; carrier gas helium.

**Kinetic measurement procedure:**
In a glovebox, 4 (23 mg, 0.036 mmol) and anthracene (internal standard, 69 mg, 0.49 mmol) were dissolved in 5 mL of C6D6 (ca. 0.0072 M in catalyst). A portion (13 uL) of this solution was added to a J. Young NMR tube followed by C6D6 (570 uL) and olefin (10 uL, 0.095 mmol). The tube was quickly sealed, removed from the glovebox, cooled to -78 °C and freeze-pump-thawed (x3). After the final freeze-pump-thaw cycle, the NMR tube was backfilled with an atmosphere of ethylene, sealed, and allowed to warm to RT. An initial NMR spectrum was taken at RT to get initial concentrations after which the tube was placed in a 50 °C oil bath. Over a period of ca. 24 h the NMR tube was periodically removed from the oil bath and the reaction was analyzed by NMR spectrometry. The ethenolysis of cis-5-decene reached a maximum of 30% while that of trans-5-decene was 10%. Therefore, the first-order kinetic plots below only take into account the early stages of the reaction, before equilibrium is established.
Alternatively, at these low concentrations, the method of initial rates can be used to compute the ratio of $\frac{d[\text{cis-5-decene}]}{dt}$ to $\frac{d[\text{trans-5-decene}]}{dt}$. As shown in the table below, the ratio of the rates derived from the method of initial rates is similar to the ratio of the rate constants obtained from the linear fits in the figure above.

<table>
<thead>
<tr>
<th>$\frac{d[\text{cis-5-decene}]}{dt}$</th>
<th>$\frac{d[\text{trans-5-decene}]}{dt}$</th>
<th>ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1.5 \times 10^{-6}$ M s$^{-1}$</td>
<td>$4.3 \times 10^{-7}$ M s$^{-1}$</td>
<td>3.4</td>
</tr>
</tbody>
</table>

**GC Data Analysis for Cross Metathesis**

To obtain accurate conversion data, GC response factors for all starting materials and products (ethylene and 1-hexene excluded) were obtained and GC data was analyzed according to the literature.$^5$ Tridecane was used as an internal standard. Samples for GC analysis were obtained by adding ca. 10-30 μl of the reaction mixture to 1 ml of ethyl vinyl ether. The resulting sample was shaken, allowed to stand for 5 min, and then analyzed via GC.

GC instrument conditions: inlet temperature: 250 °C; detector temperature: 250 °C; hydrogen flow: 30 ml/min; air flow: 400 ml/min.; constant col + makeup flow: 25 ml/min. GC Method: A) 50 °C for 4 min, followed by a temperature increase of 6 °C/min to 300 °C and a subsequent isothermal period at 300 °C for 5 min. or B) 50 °C for 2 min, followed by a temperature increase of 12 °C/min to 110 °C and a subsequent isothermal period at 110 °C for 2 min. ~ a temperature increase of 6 °C/min to 115 °C and a subsequent isothermal period at 115 °C for 0.5 min. ~ a temperature increase of 5 °C/min to 140 °C. ~ a temperature increase of 12 °C/min to 210 °C and a subsequent isothermal period at 210 °C for 2 min. ~ a temperature increase of 6 °C/min to 250 °C ~ a temperature increase of 15 °C/min to 300 °C and a subsequent isothermal period at 300 °C for 5 min.

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Representative procedure for cross metathesis of 14 with cis-5-decene (Z-11) or trans-5-decene (E-11) with catalyst 4:

In a glovebox, a 5 ml vial with a magnetic stir bar was charged with cis-5-decene (370 μl, 280 mg, 2.0 mmol) or trans-5-decene (370 μl, 280 mg, 2.0 mmol), 8-nonyl acetate (210 μl, 180 mg, 1.0 mmol) and tridecane (120 μl, 92 mg, 0.50 mmol). A solution of catalyst 4 was prepared in THF. THF and the desired volume of the catalyst solution were added to the reaction mixture [THF total 1.3 mL and 4 (1.3 mg, 0.0020 mmol)]. (Before adding the catalyst, an aliquot was taken for GC analysis to check the molar ratio of each compound at the starting point.) The vial was sealed with a screw-cap and then stirred at 35 °C. After the reaction solution was allowed to stir for 6 h, an aliquot was taken for GC analysis to obtain the yield. The vessel was removed from the glovebox and left open to air, and then the reaction solution was transferred to a 50 ml flask with using ethyl vinyl ether (ca. 10 ml). After stirring overnight at room temperature, the mixture was concentrated in vacuo. The resulting mixture was separable by flash column chromatography (SiO₂; n-hexane ~ ethyl
acetate/n-hexane=1/40 ~ 1/30 ~ 1/9) to give pure 20, 14, and 12 as colorless oils. The NMR data for 20 matched literature precedence.\textsuperscript{6}

**Procedure for cross metathesis of 14 with cis-5-decene (Z-11) or trans-5-decene (E-11) with catalyst 2:** According to the above procedure, cis-5-decene (190 μl, 140 mg, 1.0 mmol) or trans-5-decene (190 μl, 140 mg, 1.0 mmol), 8-nonlyl acetate (105 μl, 90 mg, 0.5 mmol) and tridecane (60 μl, 46 mg, 0.25 mmol) were added to a 5 mL vial. A solution of catalyst 2 was prepared in THF. THF and the desired volume of the catalyst solution were added to the reaction mixture [THF total 0.65 mL and 2 (8.2 mg, 0.013 mmol)]. These reactions were worked up according to the above procedure.

![Reaction diagram](image)

**Synthesis of Z-12**

In a glovebox, a 20 ml vial was charged with 14 (3.2 g, 17 mmol) and 4 (22 mg, 0.035 mmol) and THF (6.0 ml). The vial was sealed with a screw-cap and then stirred at 35 °C for 7.5 h. The vessel was removed from the glovebox and left open to air, and then the reaction solution was transferred to a 50 ml flask with using ethyl vinyl ether (ca. 10 ml). After stirring for overnight at room temperature, the mixture was concentrated in vacuo. The resulting residue was purified by flash column chromatography (SiO2; ethyl acetate/n-hexane=1/50 ~ 1/20 ~ 1/4) to give pure 12 (2.5 g, 7.3 mmol, 84% yield, 75 %Z) as a colorless oil. The NMR data for 12 matched that reported earlier in the supporting information.

![Reaction diagram](image)

**Representative procedure for cross metathesis of cis-5-decene (Z-11) or trans-5-decene (E-11) with 12 without ethylene in the presence of catalyst 4:**

In a glovebox, a 5 ml vial with a magnetic stir bar was charged with cis-5-decene (95 μl, 70 mg, 0.5 mmol) or trans-5-decene (95 μl, 70 mg, 0.5 mmol), 12 (170 mg, 0.50 mmol, 75 %Z) and tridecane (61 μl, 46 mg, 0.25 mmol). A solution of catalyst 4 was prepared in THF. THF and the desired volume of the catalyst solution were added to reaction mixture [THF total

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675 μl and 4 (3.2 mg, 0.0050 mmol)]. (Before adding the catalyst, an aliquot was taken for GC analysis to check the molar ratio of each compound at the starting point.) The vial was sealed with a screw-cap and then stirred at 35 °C. After the reaction solution was allowed to stir for 2 h, an aliquot was taken for GC analysis to obtain the yield. The vessel was removed from the glovebox and left open to air, and then the reaction solution was transferred to a 50 ml flask with using ethyl vinyl ether (ca. 10 ml). After stirring for overnight at room temperature, the mixture was concentrated in vacuo. The resulting mixture was separable by flash column chromatography (SiO2; n-hexane ~ ethyl acetate/n-hexane=1/40 ~ 1/30 ~ 1/9) to give pure 20, 14, and 12 as colorless oils.

**Procedure for cross metathesis of cis-5-decene (Z-11) or trans-5-decene (E-11) with 12 without ethylene in the presence of catalyst 2:**

In a glovebox, a 5 ml vial with a magnetic stir bar was charged with cis-5-decene (95 μl, 70 mg, 0.5 mmol) or trans-5-decene (95 μl, 70 mg, 0.5 mmol), 12 (170 mg, 0.50 mmol, 75 %Z) and tridecane (61 μl, 46 mg, 0.25 mmol). A solution of catalyst 4 was prepared in THF. THF and the desired volume of the catalyst solution were added to reaction mixture [THF total 675 μl and 2 (8.2 mg, 0.013 mmol)]. These reactions were worked up according to the above procedure.

**Representative procedure for cross metathesis of cis-5-decene (Z-11) or trans-5-decene (E-11) with 12 with ethylene in the presence of catalyst 4:**

In a glovebox, a 5 ml vial with a magnetic stir bar was charged with cis-5-decene (94 μl, 70 mg, 0.50 mmol) or trans-5-decene (94 μl, 70 mg, 0.50 mmol), 12 (170 mg, 0.50 mmol, 75 %Z) and tridecane (61 μl, 46 mg, 0.25 mmol). A solution of catalyst 4 was prepared in THF. THF and the desired volume of the catalyst solution were added to reaction mixture [THF total 675 μl and 4 ((3.2 mg, 0.0050 mmol))]. (Before adding the catalyst, an aliquot was taken for GC analysis to check the molar ratio of each compound at the starting point.) The reaction solution was sealed with a screw-cap septum top, removed from the glovebox, equipped with an ethylene balloon, and then purged with ethylene before heating. After the reaction solution equipped with the ethylene balloon was allowed to stir at 35 °C for 2 h, the vial was brought in the glovebox again. The reaction mixture was stirred at 35 °C while open to the glovebox atmosphere. After the reaction solution was allowed to stir for 4.5 h,
an aliquot was taken for GC analysis to obtain the yield. The vessel was removed from the glovebox and left open to air, and then the reaction solution was transferred to a 50 ml flask with using ethyl vinyl ether (ca. 10 ml). After stirring for overnight at room temperature, the mixture was concentrated *in vacuo*. The resulting mixture was separable by flash column chromatography (SiO$_2$; *n*-hexane ~ ethyl acetate/*n*-hexane=1/40 ~ 1/30 ~ 1/9) to give pure 20, 14, and 12 as colorless oils.
Figure S1. $^1$H NMR (500 MHz) spectrum of 12 in CDCl$_3$. 

S16
Figure S2. $^{13}$C NMR (126 MHz) spectrum of 12 in CDCl$_3$. 
Figure S3. $^1$H-$^{13}$C HSQC of 12 in CDCl$_3$. 
Figure S4. $^1$H NMR (500 MHz) spectrum of 15 in acetone-$d_6$. 
S19
Figure S5. $^{13}$C NMR (126 MHz) spectrum of 15 in CDCl$_3$. 
Figure S6. $^1$H-$^{13}$C HSQC of 15 in CDCl$_3$. 

S21
Figure S7. $^1$H NMR (500 MHz) spectrum of S5 in CDCl$_3$. S22
Figure S8. $^{13}$C NMR (126 MHz) spectrum of S5 in CDCl$_3$. 

S23
Figure S9. $^1$H NMR (500 MHz) spectrum of 16 in CDCl$_3$.
Figure S10. $^{13}$C NMR (126 MHz) spectrum of 16 in CDCl$_3$. 
Figure S11. $^{1}$H–$^{13}$C HSQC of 16 in CDCl$_3$. 

S26
Figure S12. $^1$H NMR (500 MHz) spectrum of S7 in CDCl$_3$. 

S27
Figure S13. $^{13}$C NMR (126 MHz) spectrum of S7 in CDCl$_3$. 

S28
Figure S14. $^1$H NMR (500 MHz) spectrum of S8 in C$_6$D$_6$. 

S29
Figure S15. $^{13}$C NMR (126 MHz) spectrum of S8 in CDCl$_3$. 
S30
Figure S16. $^1$H NMR (500 MHz) spectrum of 17 in CDCl$_3$.
Figure S17. $^{13}$C NMR (126 MHz) spectrum of 17 in CDCl$_3$. 

S32
Figure S18. $^1$H-$^{13}$C HSQC of 17 in CDCl$_3$. 
Figure S19. $^1$H NMR (500 MHz) spectrum of 18 in CDCl$_3$. 

S34
Figure S20. $^{13}$C NMR (126 MHz) spectrum of 18 in CDCl$_3$. 
S35
Figure S21. $^1$H-$^{13}$C HSQC of 18 in CDCl$_3$. 
Figure S22. $^1$H NMR (500 MHz) spectrum of the purely E-isomer of 11 in CDCl$_3$. 
Figure S23. $^1$H NMR (500 MHz) spectrum of the purely $E$-isomer of 12 in CDCl$_3$. 

S38