

Supporting Information for

General catalyst control of the monoisomerization of 1-alkenes to *trans*-2-alkenes

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Table of Contents

I. General experimental	S1-S2
II. Preparation and characterization of 1 and 3	S2-S5
III. Spectroscopic data for pure authentic alkene isomers	S6
IV. Optimization of conditions	S7-S14
V. Manuscript Table 1: Data for entries 1, 2, 3, 4, 5, and 6 and footnote j	S14-S35
VI. Manuscript Table 1: Data for entries 1a and 2a, control experiments showing differences between Cp*Ru and CpRu catalysts 1 + 3 and 2a	S36-S38
VII. Manuscript Table 1: Data for entries 2e and 2f, control experiments with complexes lacking N-heterocyclic phosphine ligand	S38-S45
VIII. Manuscript Table 2: Data	S45-S52
IX. Data for control experiments showing reaction of Cp*Ru catalyst 1 + 3 and internal alkenes	S53-S56

I. General Experimental

Reactions were performed under dry nitrogen, using a combination of Schlenk line and glovebox techniques. Acetone-*d*₆ received from Cambridge Isotope Labs was further deoxygenated by bubbling nitrogen gas through the liquid. NMR tube reactions were performed in resealable NMR tubes (J. Young).

Unless otherwise specified, NMR data were measured at 30 °C. Varian spectrometers were used: a 500-MHz INOVA (500 MHz listed below for ¹H = 499.940 MHz and 125.7 MHz for ¹³C = 125.718 MHz), and a 400-MHz Varian NMR-S (400 MHz listed below for ¹H = 399.763 MHz and 100 MHz for ¹³C = 100.525 MHz).

^1H and ^{13}C NMR chemical shifts are reported in ppm, referenced to solvent resonances (^1H NMR: δ 2.05 for $\text{CHD}_2\text{COCD}_3$ and ^{13}C NMR: δ 29.92 for CD_3COCD_3). ^1H NMR signals are given followed by multiplicity, coupling constants J in Hertz, integration in parentheses. For complex coupling patterns, the first coupling constant listed corresponds to the first splitting listed, e.g. for (dt, $J = 3.2, 7.9$, 1H) the doublet exhibits the 3.2-Hz coupling constant.

Gas chromatography (GC) analyses were performed on an Agilent 7820A apparatus with (5%-phenyl)-methylpolysiloxane column (HP-5 30 m x 0.32 mm, film 0.25 micron). Column flow rate 3 mL min^{-1} make up flow 25 mL min^{-1} , H_2 flow 30 mL min^{-1} , air flow 300 mL min^{-1} , inlet temperature 275 $^\circ\text{C}$, column temperature program is specified for each experiment.

Elemental analyses were performed at NuMega Laboratories (San Diego).

II. Preparation and characterization of **1** and **3**

tris(acetonitrile)Pentamethylcyclopentadienylruthenium (II) hexafluorophosphate (116.9 mg, 0.2317 mmol) was weighed in a scintillation vial equipped with a magnetic stir bar in a glove box, and deoxygenated acetone (6 mL) was added. In a separate vial, the requisite phosphine (59.4 mg, 0.2336 mmol) was weighed and deoxygenated acetone (1 mL) was added. The phosphine dissolved in acetone was added dropwise to the ruthenium complex solution, and deoxygenated acetone was used to rinse the vial. The mixture was allowed to stir in the glovebox at ambient temperature overnight, though formation of **3** occurs within 15 min [see below]. The solvent was evaporated forming a foam, to which was added acetone. The process was repeated four times within 2 h. After concentration, the residue was stored under vacuum to afford a yellow-brown foam (152.6 mg vs. 156.7 mg theoretical yield for pure **1** and 166.3 mg for pure **3**; given composition, yield is about 93%).

Analysis by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy showed chelate complex **1** and nonchelated complex **3** in a ratio of ca. 1 to 3. Despite all efforts (in other experiments) at increasing the proportion of **1**, **3** was always the major component. The ratio obtained varied somewhat from batch to batch, from about 1 to 3 to 1 to 5. Not all NMR signals for **1** could be determined with certainty because at any temperature used between +30 and -70 $^\circ\text{C}$, at least some of the peaks were broadened in either or both ^1H and ^{13}C NMR spectra. At -20 $^\circ\text{C}$ all resonances except for those involving the iso-propyl groups on P could be identified using 1D and 2D spectra, which are summarized graphically in Fig. S1. Combustion analysis for a sample from another preparation - Found: C, 45.67; H, 6.62; N, 7.45. Anal. Calcd. for a 1:3 mixture of **1** and **3**: C, 46.33; H, 6.73; N, 7.41. Anal. Calcd. for pure **1**: C, 46.15; H, 6.70; N, 6.21. Anal. Calcd. for pure **3**: C, 46.86; H, 6.74; N, 7.81.

Chelate (**1**) partial ^1H NMR (500 MHz, acetone- d_6 , $-20\text{ }^\circ\text{C}$) δ 6.97 (s, 1H), 3.73 (s, 3H), 2.45 (s, 3H), 1.71 (d, $J = 1.5$, 15H), 1.29 ppm (s, 9H). Partial $^{13}\text{C}\{^1\text{H}\}$ NMR (125.73 MHz, acetone- d_6 , $-20\text{ }^\circ\text{C}$) δ 153.1 (d, $J = 14.3$), 148.3 (d, $J = 28.5$), 127.6, 119.8, 82.2 (d, $J = 2.3$), 34.7, 31.9, 29.6 (overlapping with one peak from solvent, but identified by HMBC crosspeak with proton signal at 1.29 ppm), 11.2, 3.7 ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (202.38 MHz, acetone- d_6 , $-20\text{ }^\circ\text{C}$) δ 28.3 ppm (s).

Bis acetonitrile complex (**3**) partial ^1H NMR (500 MHz, acetone- d_6 , $-20\text{ }^\circ\text{C}$) δ 7.01 (s, 1H), 3.67 (s, 3H), 2.64 (s, 6H), 1.36 (s, 15H), 1.24 ppm (s, 9H). Partial ^{13}C NMR (125.73 MHz, acetone- d_6 , $-20\text{ }^\circ\text{C}$) δ 151.7 (d, $J = 7.8$), 142.5 (d, $J = 58.0$), 128.1 (sl br s), 119.4, 86.8 (d, $J = 1.8$), 34.0 (d, $J = 0.9$), 32.3, 30.4, 8.9, 4.0 ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (202.38 MHz, acetone- d_6 , $-20\text{ }^\circ\text{C}$) δ 36.7 ppm (s).

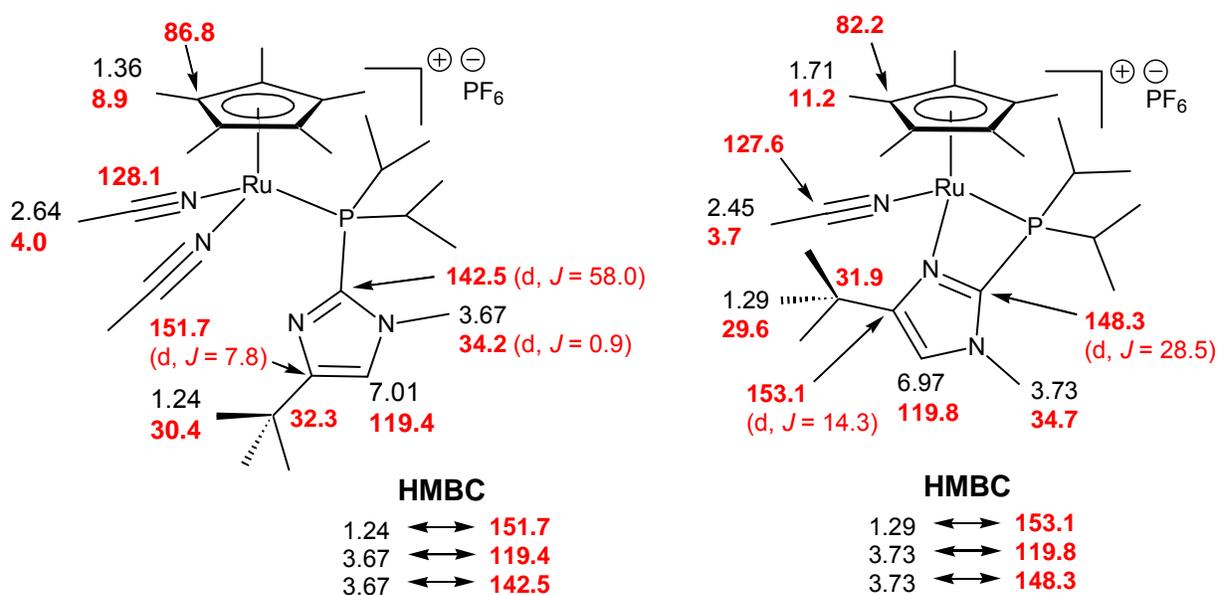


Figure S1. Graphical summary of ^1H (black) and ^{13}C (red, bold) NMR data for **1** and **3**, observed as a mixture in acetone- d_6 at $-20\text{ }^\circ\text{C}$. Selected key gHMBC crosspeaks allowing identification of imidazole carbons are shown.

Rate of phosphine binding

In a glove box to a resealable J. Young tube was added $[\text{Cp}^*\text{Ru}(\text{CH}_3\text{CN})_3]\text{PF}_6$ (20.4 mg, 0.0404 mmol) and deoxygenated acetone- d_6 (900 μL). To the ruthenium precursor solution was added the requisite phosphine (10.9 mg, 0.0428 mmol) in deoxygenated acetone- d_6 (200 μL) and allowed to mix and proceed at room temperature. The reaction was evaluated via ^1H and ^{31}P NMR after 15 min, from which it was concluded that formation of **3** was complete.

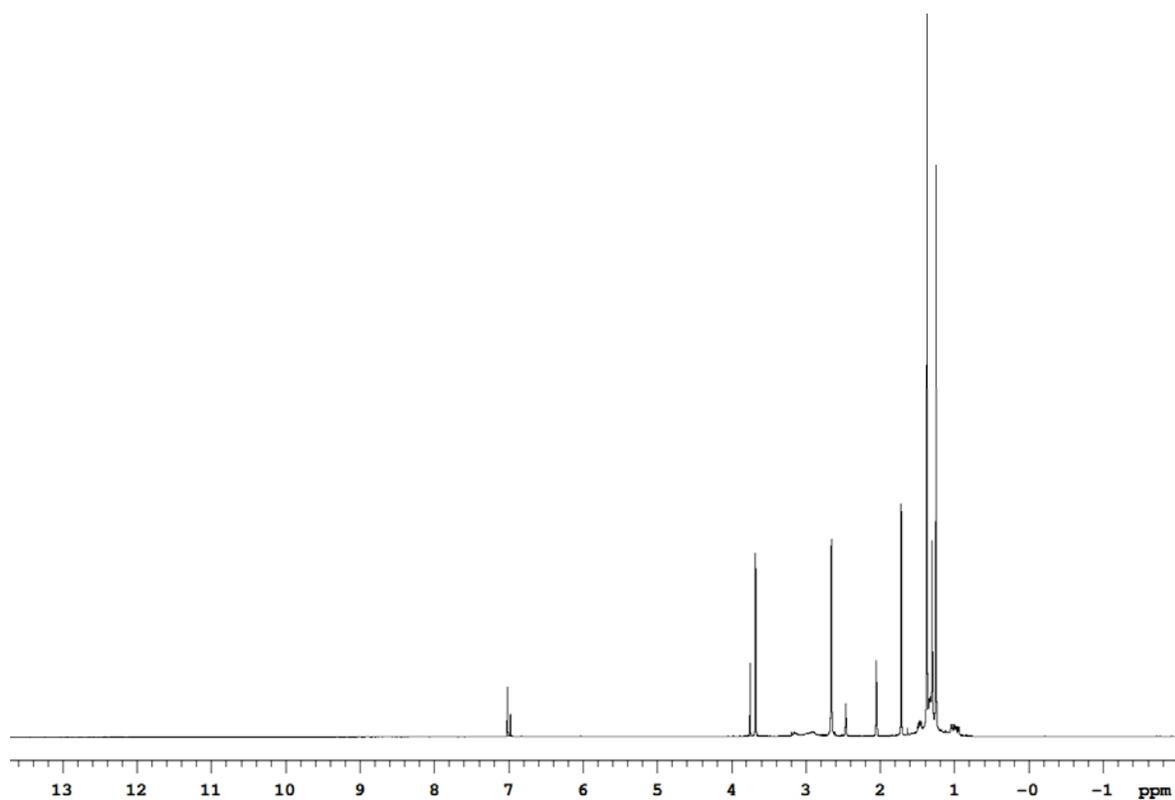


Figure S2. ^1H NMR spectrum of **1 + 3** at $-20\text{ }^\circ\text{C}$ (500 MHz, acetone- d_6).

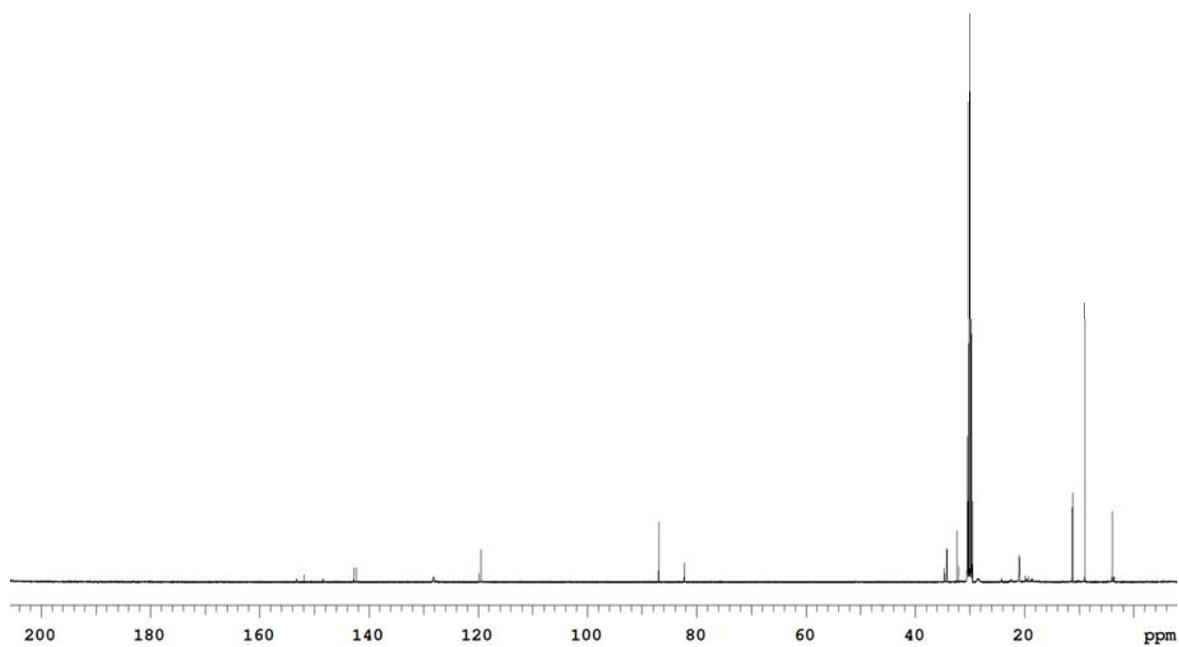


Figure S3. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum **1 + 3** at $-20\text{ }^\circ\text{C}$ (125.7 MHz, acetone- d_6).

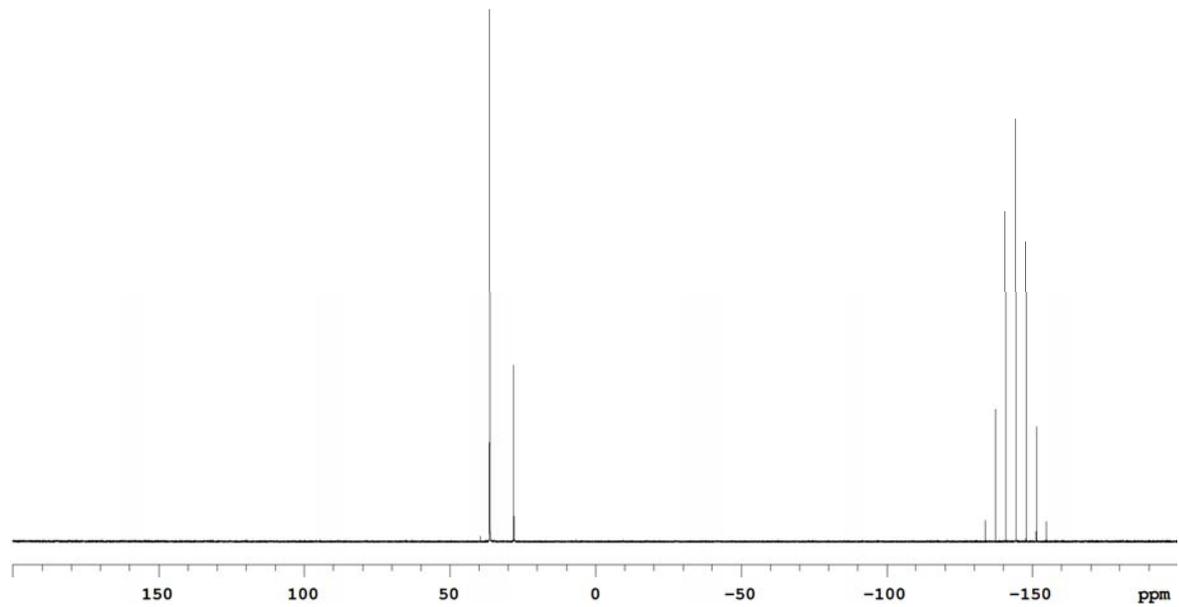
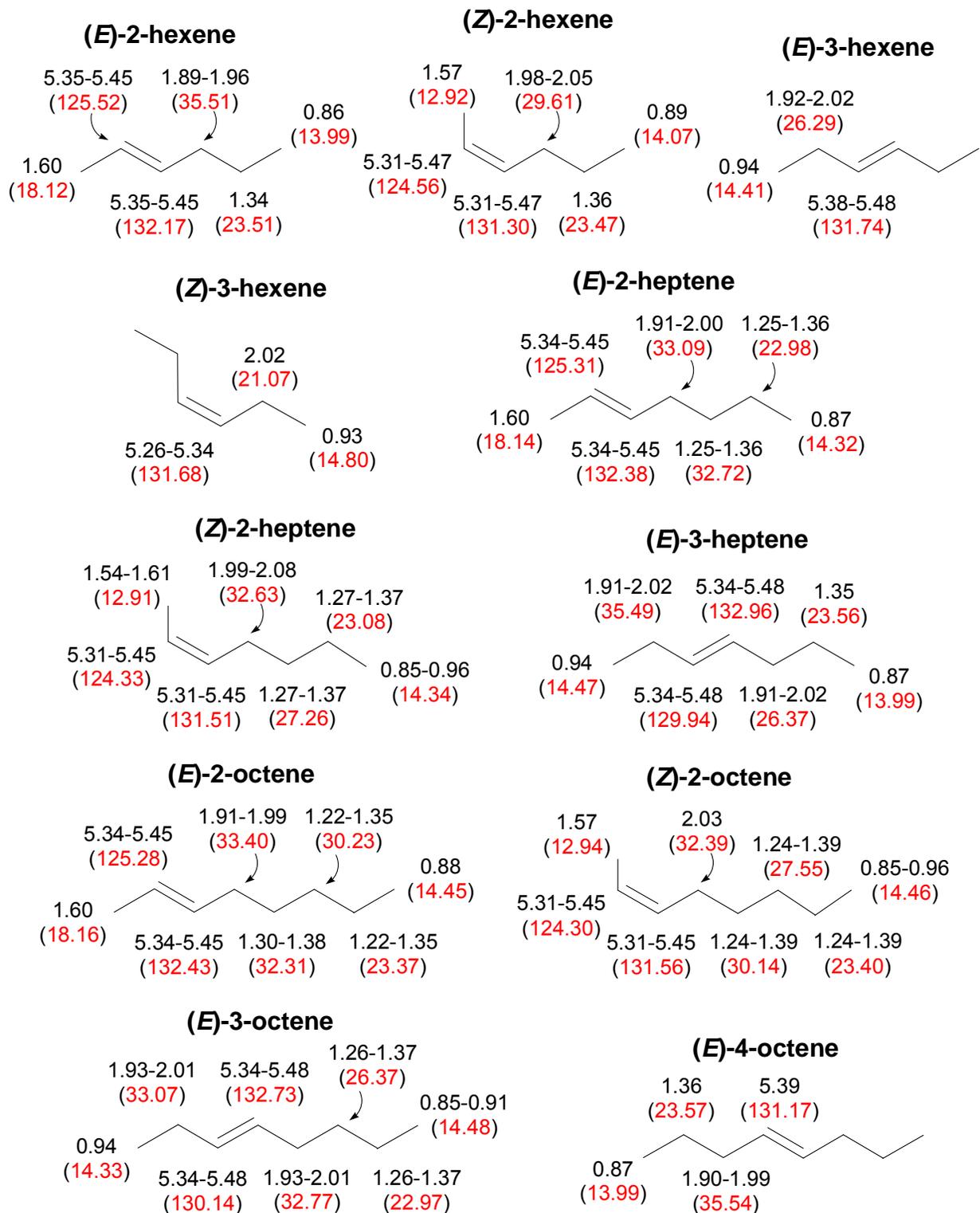


Figure S4. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **1 + 3** at $-20\text{ }^\circ\text{C}$ (202.4 MHz, acetone- d_6).

III. Spectroscopic data for pure authentic isomeric alkenes

(¹H 500 MHz, ¹³C 125.7 MHz, acetone-d₆)



IV. Optimization of conditions

General procedure for catalytic reactions – example at 5 mol%

In a glovebox, internal standard $(\text{Me}_3\text{Si})_4\text{C}$ (small weighed amount, typically 0.5 mg) and substrate (0.50 mmol) were combined with acetone- d_6 (~700 μL), and an initial NMR spectrum was acquired. Back in the glovebox, to this mixture was added catalyst **1 + 3** (19.0 mg, 0.025 mmol; 5 mol%) followed by enough acetone- d_6 to reach a final volume of 1.0 mL. The reaction was allowed to proceed at room temperature, however if the mixture was heated in an oil bath, it was heated for the times given. Unless otherwise specified, spectra were acquired at NMR probe temperature of 30 $^\circ\text{C}$.

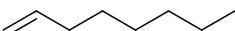
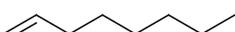
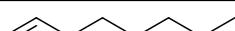
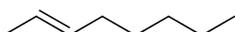
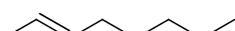
The value of the integral for the singlet due to the internal standard, $(\text{Me}_3\text{Si})_4\text{C}$, was set equal to 10.00 integral units in each case. Data were acquired using either a Varian 400 MHz or 500 MHz spectrophotometer, with sixteen 15° pulses and 20 sec delays between pulses. Tables show key NMR resonances which could be used to reliably determine yields. Other ^1H resonances for starting material and product overlapped and so were not used. Approximate limit of detection was estimated at 0.2-0.5% for signals well-separated from other signals, in the absence of overlap.

IV-1. Isomerization of 1-octene using 5 mol% catalyst at room temperature in acetone- d_6 . Following the general procedure, 1-octene (57.0 mg, 0.508 mmol) and catalyst **1 + 3** (19.3 mg, 0.0254 mmol, 5.0 mol%) were used. The reaction was conducted at room temperature.

For 1-octene in the mixture: ^1H NMR (500 MHz, acetone- d_6) δ 5.80 (tdd, $J = 7.0, 10.0, 17.5$, 1H), 4.97 (dtd, $J = 1.5, 2.0, 17.5$, 1H), 4.89 (tdd, $J = 1.0, 2.0, 10.0$, 1H), 1.99-2.07 (m, 2H), 1.34-1.42 (m, 2H), 1.24-1.34 (m, 6H), 0.88 ppm (t, $J = 7.0$, 3H). ^{13}C NMR (125.73 MHz, acetone- d_6) δ 139.90, 114.71, 34.61, 32.59, 29.81, 29.66, 23.41, 14.44 ppm.

For the (*E*)-2-octene in the mixture: ^1H NMR (500 MHz, acetone- d_6) δ 5.34-5.46 (m, 2H), 1.91-1.99 (m, 2H), 1.60 (~d of narrow m, $J \approx 4$, 3H), 1.22-1.38 (m, 6H), 0.87 ppm (t, $J = 7.0$, 3H). ^{13}C NMR (125.73 MHz, acetone- d_6) δ 132.42, 125.29, 33.33, 32.23, 30.15, 23.29, 18.11, 14.40 ppm.

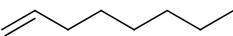
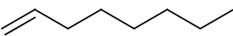
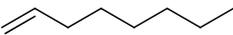
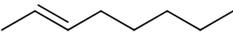
Table S-IV-1. Isomerization of 1-octene using 5 mol% catalyst at room temperature in acetone-*d*₆.

	Measured integrals in arbitrary units relative to internal standard = 10.0 units and (in bold) derived per cent yields of products and amount of starting 1-alkene					
Time	0 h	26 h	50 h	74 h	97 h	121 h
 (5.80 ppm)	68.18	18.64	8.40	4.47	2.70	1.93
 (4.97 ppm)	69.85	18.91	8.55	4.63	2.66	2.10
 (4.89 ppm)	68.86	18.71	8.35	4.50	2.64	2.04
units per proton ^a	68.96	18.75	8.43	4.53	2.67	2.02
% starting material remaining ^b	100	27.2	12.2	6.6	3.9	2.9
 (5.34-5.45 ppm)	0	99.38	119.32	129.70	132.82	133.27
 (1.60 ppm)	0	152.18	184.83	199.38	203.88	203.56
units per proton ^a	0	50.31	60.83	65.82	67.34	67.37
% yield of product ^c	0	73.0	88.2	95.4	97.7	97.7

^aCalculated by taking the average of integrations of the specified resonances. ^bCalculated by dividing units per proton of starting material at time indicated by units per proton value at hour 0. ^cCalculated by dividing units per proton of product at time indicated by the units per proton value of starting material at hour 0.

IV-2. Isomerization of 1-octene using 4 mol% catalyst at room temperature in acetone-*d*₆. Following the general procedure, 1-octene (56.9 mg, 0.507 mmol) and catalyst **1 + 3** (14.8 mg, 0.021 mmol, 4.1 mol%) were used. The reaction was conducted at room temperature.

Table S-IV-2. Isomerization of 1-octene using 4 mol% catalyst at room temperature in acetone- d_6 .

	Measured integrals in arbitrary units relative to internal standard = 10.0 units and (in bold) derived per cent yields of products and amount of starting 1-alkene				
Time	0 h	24 h	48 h	72 h	96 h
 (5.80 ppm)	45.55	11.57	4.43	1.99	1.26
 (4.97 ppm)	46.25	11.66	4.47	2.01	1.39
 (4.89 ppm)	46.45	11.61	4.39	1.98	1.30
units per proton ^a	46.08	11.61	4.43	1.99	1.32
% starting material remaining ^b	100	25.2	9.6	4.3	2.8
 (5.34-5.46 ppm)	0	67.72	84.99	87.92	88.99
units per proton ^a	0	33.86	42.50	43.96	44.49
% yield of product ^c	0	73.5	92.2	95.4	96.6

^aCalculated by taking the average of integrations of the specified resonances. ^bCalculated by dividing units per proton of starting material at time indicated by units per proton value at hour 0. ^cCalculated by dividing units per proton of product at time indicated by the units per proton value of starting material at hour 0.

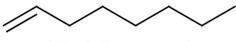
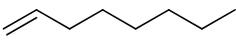
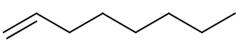
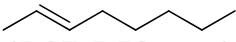
IV-3. Isomerization of 1-octene using 4 mol% catalyst at room temperature in CD_2Cl_2 . Following the general procedure, 1-octene (54.9 mg, 0.489 mmol) and catalyst **1 + 3** (13.5 mg, 0.019 mmol, 3.9 mol%) were used, but deoxygenated methylene chloride- d_2 was used. The reaction was conducted at room temperature.

For 1-octene in the mixture: 1H NMR (500 MHz, CD_2Cl_2) δ 5.82 (tdd, $J = 6.5, 10.0, 17.0, 1H$), 5.00 (dtd, $J = 1.5, 2.0, 17.0, 1H$), 4.93 (tdd, $J = 1.0, 2.0, 10.0, 1H$), 2.06 (td, $J = 7.0, 7.0, 2H$), 1.35-1.45 (m, 2H), 1.24-1.35 (m, 6H), 0.91 ppm (t, $J = 7.0, 3H$). ^{13}C NMR (125.73 MHz, CD_2Cl_2) δ 139.99, 114.52, 34.57, 32.51, 29.73, 29.60, 23.38, 14.56 ppm.

For the (*E*)-2-octene in the mixture: 1H NMR (500 MHz, CD_2Cl_2) δ 5.37-5.50 (m, 2H), 1.93-2.01 (m, 2H), 1.64 (~d of narrow m, $J \approx 5, 3H$), 1.23-1.41 (m, 6H), 0.90 ppm (t,

$J = 7.0, 3\text{H}$). ^{13}C NMR (125.73 MHz, CD_2Cl_2) δ 132.35, 125.10, 33.23, 32.16, 30.02, 23.23, 18.26, 14.48 ppm.

Table S-IV-3. Isomerization of 1-octene using 4 mol% catalyst at room temperature in CD_2Cl_2 .

	Measured integrals in arbitrary units relative to internal standard = 10.0 units and (in bold) derived per cent yields of products and amount of starting 1-alkene				
Time	0 h	24 h	48 h	72 h	311 h
 (5.82 ppm)	46.22	32.89	23.64	18.38	3.22
 (5.00 ppm)	47.07	32.66	23.55	17.68	2.96
 (4.93 ppm)	46.71	32.83	23.40	17.78	2.86
units per proton ^a	46.67	32.79	23.53	17.95	3.01
% starting material remaining ^b	100	70.3	50.4	38.5	6.5
 (5.37-5.50 ppm)	0	28.66	45.30	58.12	87.60
units per proton ^a	0	14.33	22.65	29.06	43.80
% yield of product ^c	0	30.7	48.5	62.3	93.9

^aCalculated by taking the average of integrations of the specified resonances. ^bCalculated by dividing units per proton of starting material at time indicated by units per proton value at hour 0. ^cCalculated by dividing units per proton of product at time indicated by the units per proton value of starting material at hour 0.

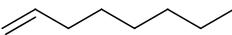
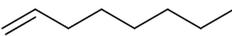
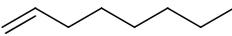
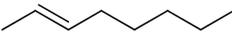
IV-4. Isomerization of 1-octene using 4 mol% catalyst in CD_3NO_2 at 35 °C.

Following the general procedure, 1-octene (57.1 mg, 0.509 mmol) and catalyst **1 + 3** (15.4 mg, 0.022 mmol, 4.3 mol%) were used, except that deoxygenated nitromethane- d_3 was used (with trace amounts of acetone- d_6 for solubility reasons). The reaction was conducted at 35 °C.

For 1-octene in the mixture: ^1H NMR (500 MHz, CD_3NO_2) δ 5.82 (tdd, $J = 6.5, 10.0, 17.0, 1\text{H}$), 4.98 (dtd, $J = 1.5, 1.5, 17.0, 1\text{H}$), 4.90 (tdd, $J = 1.0, 1.0, 10.0, 1\text{H}$), 2.04 (~q, $J = 7.0, 2\text{H}$), 1.34-1.42 (m, 2H), 1.24-1.34 (m, 6H), 0.88 ppm (t, $J = 7.0, 3\text{H}$). ^{13}C NMR (125.73 MHz, CD_3NO_2) δ 140.55, 114.95, 34.95, 32.92, 30.14, 30.01, 23.75, 14.69 ppm.

For the (*E*)-2-octene in the mixture: ^1H NMR (500 MHz, CD_3NO_2) δ 5.36-5.48 (m, 2H), 1.92-1.99 (m, 2H), 1.61 (~d of narrow m, $J \approx 5$, 3H), 1.22-1.38 (m, 6H), 0.88 ppm (t, $J = 7.0$, 3H). ^{13}C NMR (125.73 MHz, CD_3NO_2) δ 133.02, 125.83, 33.68, 32.62, 30.49, 23.66, 18.32, 14.61 ppm.

Table S-IV-4. Isomerization of 1-octene using 4 mol% catalyst in CD_3NO_2 at 35 °C.

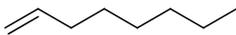
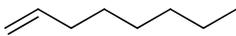
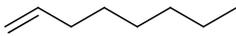
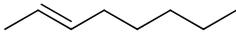
Time	Measured integrals in arbitrary units relative to internal standard = 10.0 units and (in bold) derived per cent yields of products and amount of starting 1-alkene				
	0 h	1 h	2 h	5 h	24 h
 (5.82 ppm)	62.75	48.94	34.56	20.60	2.45
 (4.98 ppm)	63.67	49.28	34.89	21.51	2.27
 (4.90 ppm)	63.57	48.60	35.01	20.30	2.23
units per proton ^a	63.33	48.94	34.82	20.80	2.32
% starting material remaining ^b	100	77.3	55.0	32.8	3.6
 (5.36-5.48 ppm)	0	31.96	57.11	88.43	122.41
units per proton ^a	0	15.98	28.56	44.22	61.21
% yield of product ^c	0	25.2	45.1	69.8	96.6

^aCalculated by taking the average of integrations of the specified resonances. ^bCalculated by dividing units per proton of starting material at time indicated by units per proton value at hour 0. ^cCalculated by dividing units per proton of product at time indicated by the units per proton value of starting material at hour 0.

IV-5. Isomerization of 1-octene using 4 mol% catalyst at 35 °C in acetone-*d*₆.

Following the general procedure, 1-octene (56.1 mg, 0.500 mmol) and catalyst **1** + **3** (14.1 mg, 0.020 mmol, 4.0 mol%) were used. The reaction was conducted at 35 °C.

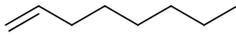
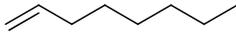
Table S-IV-5. Isomerization of 1-octene using 4 mol% catalyst at 35 °C in acetone-*d*₆.

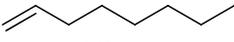
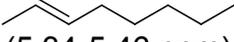
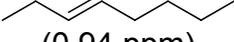
	Measured integrals in arbitrary units relative to internal standard = 10.0 units and (in bold) derived per cent yields of products and amount of starting 1-alkene				
Time	0 h	1 h	2 h	5 h	24 h
 (5.80 ppm)	143.61	118.15	90.96	60.22	7.78
 (4.97 ppm)	146.23	117.32	91.90	60.89	8.39
 (4.89 ppm)	148.28	117.85	92.63	60.47	7.98
units per proton ^a	146.04	117.77	91.83	60.53	8.05
% starting material remaining ^b	100	80.6	62.9	41.4	5.5
 (5.34-5.46 ppm)	0	54.71	101.77	169.60	267.15
units per proton ^a	0	27.36	50.89	84.8	133.58
% yield of product ^c	0	18.7	34.8	58.1	91.5

^aCalculated by taking the average of integrations of the specified resonances. ^bCalculated by dividing units per proton of starting material at time indicated by units per proton value at hour 0. ^cCalculated by dividing units per proton of product at time indicated by the units per proton value of starting material at hour 0.

IV-6. Isomerization of 1-octene using 2 mol% catalyst at 40 °C. Following the general procedure, 1-octene (56.9 mg, 0.51 mmol) and catalyst **1 + 3** (6.9 mg, 0.0098 mmol, 1.9 mol%) were used. The reaction was conducted at 40 °C.

Table S-IV-6. Isomerization of 1-octene using 2 mol% catalyst at 40 °C in acetone-*d*₆.

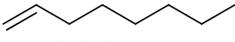
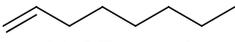
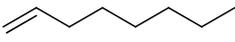
	Measured integrals in arbitrary units relative to internal standard = 10.0 units and (in bold) derived per cent yields of products and amount of starting 1-alkene					
Time	0 h	1 h	2 h	5 h	24 h	48 h
 (5.80 ppm)	58.34	50.52	42.33	27.46	3.38	1.54
 (4.97 ppm)	59.10	50.99	42.56	28.29	3.32	1.61

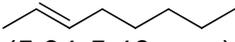
 (4.89 ppm)	58.80	51.00	43.11	28.20	3.22	1.49
units per proton ^a	58.75	50.84	42.67	27.98	3.31	1.55
% starting material remaining ^b	100	86.5	26.2	47.6	5.6	2.6
 (5.34-5.46 ppm)	0	15.88	30.77	61.47	109.58	112.89
units per proton ^a	0	7.94	15.39	30.74	54.79	56.45
% yield of product ^c	0	13.5	26.2	52.3	93.3	96.1
 (0.94 ppm)	0	0	0	0	0	4.35
units per proton ^a	0	0	0	0	0	1.45
% yield of product ^c	0	0	0	0	0	2.4

^aCalculated by taking the average of integrations of the specified resonances. ^bCalculated by dividing units per proton of starting material at time indicated by units per proton value at hour 0. ^cCalculated by dividing units per proton of product at time indicated by the units per proton value of starting material at hour 0.

IV-7. Manuscript Table 1, entry 4: Isomerization of 1-octene using 1 mol% catalyst at 40 °C in acetone-*d*₆. Following the general procedure, 1-octene (58.5 mg, 0.521 mmol) and catalyst **1 + 3** (3.9 mg, 0.0055 mmol, 1 mol%) were used. The reaction was conducted at 40 °C.

Table S-IV-7. Isomerization of 1-octene using 1 mol% catalyst at 40 °C in acetone-*d*₆.

	Measured integrals in arbitrary units relative to internal standard = 10.0 units and (in bold) derived per cent yields of products and amount of starting 1-alkene					
Time	0 h	1 h	2 h	5 h	24 h	48 h
 (5.80 ppm)	36.73	32.62	29.52	22.81	6.33	2.30
 (4.97 ppm)	36.88	33.04	30.05	23.16	6.53	2.48
 (4.89 ppm)	36.85	32.75	30.05	23.34	6.52	2.37
units per proton ^a	36.82	32.80	29.87	23.10	6.46	2.38

% starting material remaining ^b	100	89.1	81.1	62.7	17.5	6.5
 (5.34-5.46 ppm)	0	8.98	14.34	27.85	60.90	70.17
units per proton ^a	0	4.49	7.17	13.93	30.45	35.09
% yield of product ^c	0	12.2	19.5	37.8	82.7	95.3

^aCalculated by taking the average of integrations of the specified resonances. ^bCalculated by dividing units per proton of starting material at time indicated by units per proton value at hour 0. ^cCalculated by dividing units per proton of product at time indicated by the units per proton value of starting material at hour 0.

V. Manuscript Table 1: Data for entries 1, 2, 3, 4, 5, and 6 and footnote j

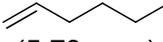
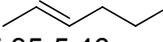
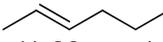
General procedure. In a glovebox, internal standard (Me₃Si)₄C (small weighed amount, typically 0.5 mg) and substrate (0.50 mmol) were combined with acetone-*d*₆ (~700 μL), and an initial NMR spectrum was acquired. Back in the glovebox, to this mixture was added catalyst **1 + 3** followed by enough acetone-*d*₆ to reach a final volume of 1.0 mL. The reaction was heated for the times given at 40 °C.

Mixtures were analyzed by ¹H NMR spectroscopy as in the optimization studies in section IV, using internal standard to get product yields. In the case of hydrocarbon alkenes (hexene, heptene, octene, decene) mixtures were also analyzed by GC for product ratios, with comparisons in the case of hexene, heptene and octene with authentic samples of 2-*E*, 2-*Z*, and 3-*E* alkenes.

V-1. Data for manuscript Table 1, entry 1. Procedure for isomerization of 1-hexene to *E*-2-hexene using 1 mol% catalyst at 40 °C in acetone-*d*₆.

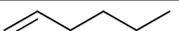
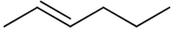
Following the general procedure, 1-hexene (42.0 mg, 0.499 mmol) and catalyst **1 + 3** (3.5 mg, 0.005 mmol, 1 mol%) were used. Reaction was conducted at 40 °C using an oil bath. At specified time points, ¹H NMR spectra were obtained and 5 μL of reaction mixture was removed under glovebox atmosphere for GC analysis. For addition of *Z*-2-hexene and *E*-3-hexene, a stock solution of 200 μL was prepared with *Z*-2-hexene (8.7 mg, 0.10 mmol) and *E*-3-hexene (8.6 mg, 0.10 mmol). 10 μL of this solution was added to the reaction point at 48 h time point.

Table S-V-1a. Yields determined by NMR in isomerization of **1-hexene** using 1 mol% catalyst at 40 °C.

	Measured integrals in arbitrary units relative to internal standard = 10.0 units and (in bold) derived per cent yields of products and amount of starting 1-alkene.				
Time	0 h	5 h	22 h	48 h	48 h with added Z-2 (1.0 %) and E-3 (1.0 %) ^a
 (5.79 ppm)	36.23	14.25	1.78	0.85	0.99
 (4.85-5.01 ppm)	73.47	29.18	3.32	1.72	1.80
units per proton ^b	36.57	14.48	1.70	0.86	0.93
% starting material remaining^c	100	39.6	4.6	2.3	2.5
 (5.35-5.46 ppm) ^d	-	44.86	70.28	70.44	72.85
 (1.60 ppm)	-	67.24	104.26	104.17	106.40 ^e
units per proton ^b	-	22.42	34.91	34.92	35.85
% of E-2^f	-	61.3	95.5	95.5	98.0
 (0.94 ppm)	-	-	2.36	4.62	6.86
units per proton ^b	-	-	0.39	0.77	1.14
% of E-3^f	-	-	1.1	2.1	3.1

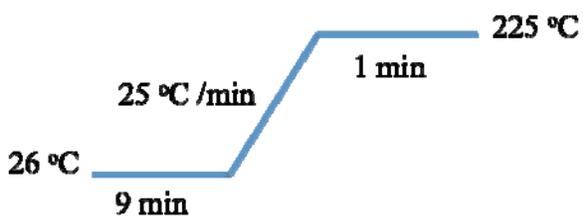
^a Spiked with 0.0051 mmol (1.0 %) of Z-2 and 0.0051 mmol (1.0 %) of E-3. ^b Calculated by taking the average of integrations of the specified resonances. ^c Calculated by dividing units per proton of starting material at time indicated by units per proton value at hour 0. ^d Includes vinylic H for E-2, E-3 and Z-2, but none of these species are present in more than 1% yield until about 24 h, where E-3-hexene is the most prevalent (2.1 % at 48 h). ^e Includes integration for Z-2 methyls (3H). ^f Calculated by dividing units per proton of product at time indicated by the units per proton value of starting material at hour 0.

Table S-V-1b. Ratios determined by GC in isomerization of **1-hexene** using 1 mol% catalyst at 40 °C.

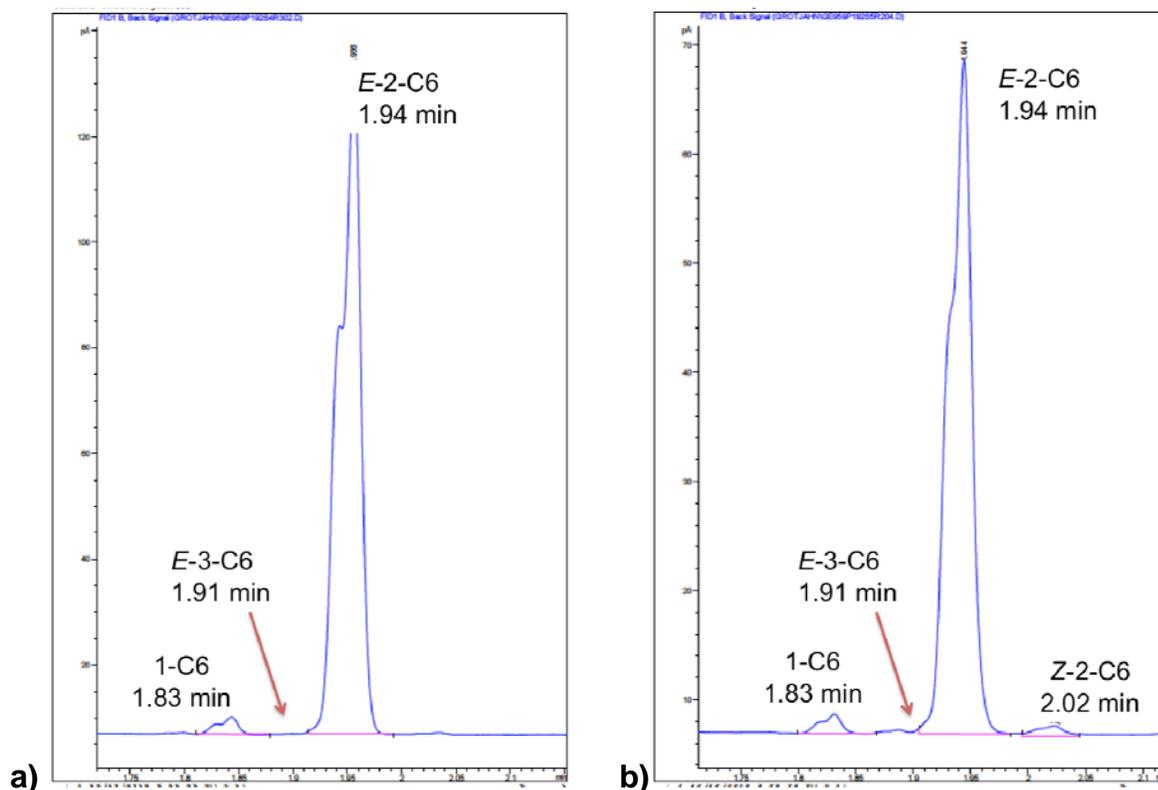
Time	5 h	22 h	48 h	48 h with added Z-2 (1.0%) and E-3 (1.0%) ^a
 (1.83 min)	39.47	2.30	4.04	2.18
% starting material remaining ^b	38.2	4.8	2.2	2.5
 (1.94 min)  (1.91 min)	63.87	45.49	174.85	84.69
% of E-2 and E-3	61.8	95.2	97.8	95.8
 (2.02 min)	0	0	0	1.55
% of Z-2 ^b	0	0	0	1.8
Total area	103.34	47.79	178.89	88.42

^a Spiked with 0.0051 mmol (1.0 %) of Z-2 and 0.0051 mmol (1.0 %) of E-3. ^b Calculated by taking the ratios of integrations of the specified retention times.

Scheme S-V-1a. Gas chromatography temperature program for C6 reaction mixtures.



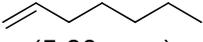
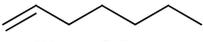
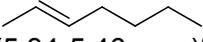
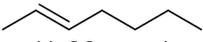
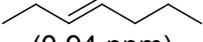
Scheme S-V-1b. Gas chromatogram of C6 reaction mixtures **a)** 48 h. **b)** 48 h with added of Z-2-hexene (1.0 %) and E-3-hexene (1.0 %).



V-2. Data for manuscript Table 1, entry 2. Procedure for isomerization of 1-heptene to *E*-2-heptene using 1 mol% catalyst at 40 °C in acetone-*d*₆.

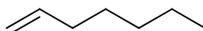
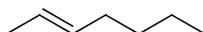
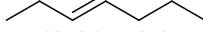
Following the general procedure, 1-heptene (49.3 mg, 0.502 mmol) and catalyst **1** + **3** (3.6 mg, 0.005 mmol, 1 mol%) were used. Reaction was conducted at 40 °C using an oil bath. At specified time points, ¹H NMR spectra were obtained and 5 μL of reaction mixture was removed under glovebox atmosphere for GC analysis. For addition of Z-2-heptene and *E*-3-heptene, stock solution of 200 μL was prepared with Z-2-heptene (9.8 mg, 0.10 mmol) and *E*-3-heptene (9.7 mg, 0.099 mmol). 10 μL of this solution was added to the reaction point at 48 h time point.

Table S-V-2a. Yields determined by NMR in isomerization of **1-heptene** using 1 mol% catalyst at 40 °C.

	Measured integrals in arbitrary units relative to internal standard = 10.0 units and (in bold) derived per cent yields of products and amount of starting 1-alkene.				
Time	0 h	5 h	22 h	48 h	48 h with added Z-2 (1.0 %) and E-3 (1.0 %) ^a
 (5.80 ppm)	62.02	27.75	3.84	1.56	1.56
 (4.90-4.97 ppm)	126.71	56.37	7.50	3.11	3.25
units per proton ^b	62.91	28.04	3.78	1.56	1.60
% starting material remaining^c	100	44.6	6.0	2.5	2.6
 (5.34-5.46 ppm) ^d	-	67.99	117.49	120.24	123.48
 (1.60 ppm)	-	103.91	176.11	180.46	181.44 ^e
units per proton ^b	-	34.38	58.72	60.14	60.98
% of E-2^f	-	54.6	93.3	95.6	96.9
 (0.94 ppm)	-	-	3.07	5.52	6.73
units per proton ^b	-	-	1.02	1.84	2.24
% of E-3^f	-	-	1.6	2.9	3.6

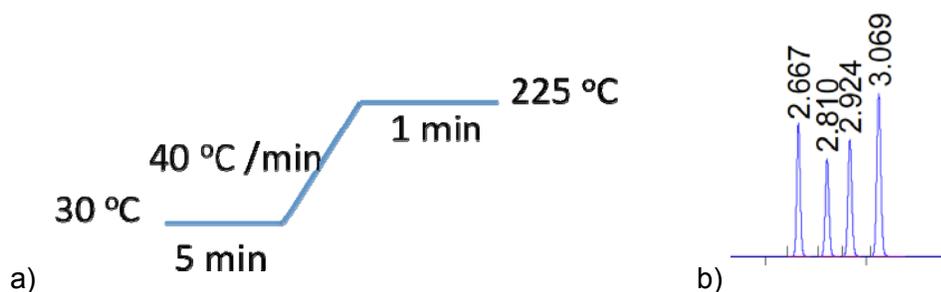
^a Spiked with 0.005 mmol (1.0 %) of Z-2 and 0.0050 mmol (1.0 %) of E-3. ^b Calculated by taking the average of integrations of the specified resonances. ^c Calculated by dividing units per proton of starting material at time indicated by units per proton value at hour 0. ^d Includes vinylic H for E-2, E-3 and Z-2, but none of these species are present in more than 1% yield until about 24 h, where E-3-heptene is the most prevalent (2.9 % at 48 h). We note that if one uses only the δ 1.60 ppm resonance value at 48 h, one still gets 95.6% yield, which matches GC results (Table S-V-2b). ^e Includes integration for Z-2 methyls (3H). ^f Calculated by dividing units per proton of product at time indicated by the units per proton value of starting material at hour 0.

Table S-V-2b. Ratios determined by GC in isomerization of **1-heptene** using 1 mol% catalyst at 40 °C.

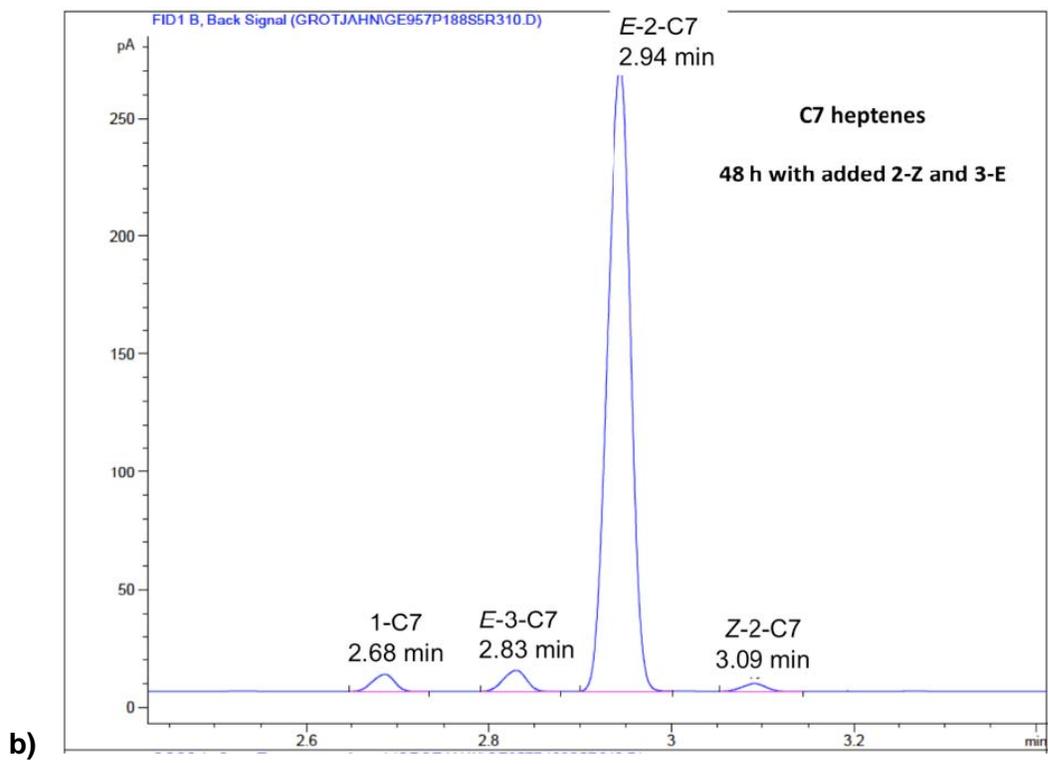
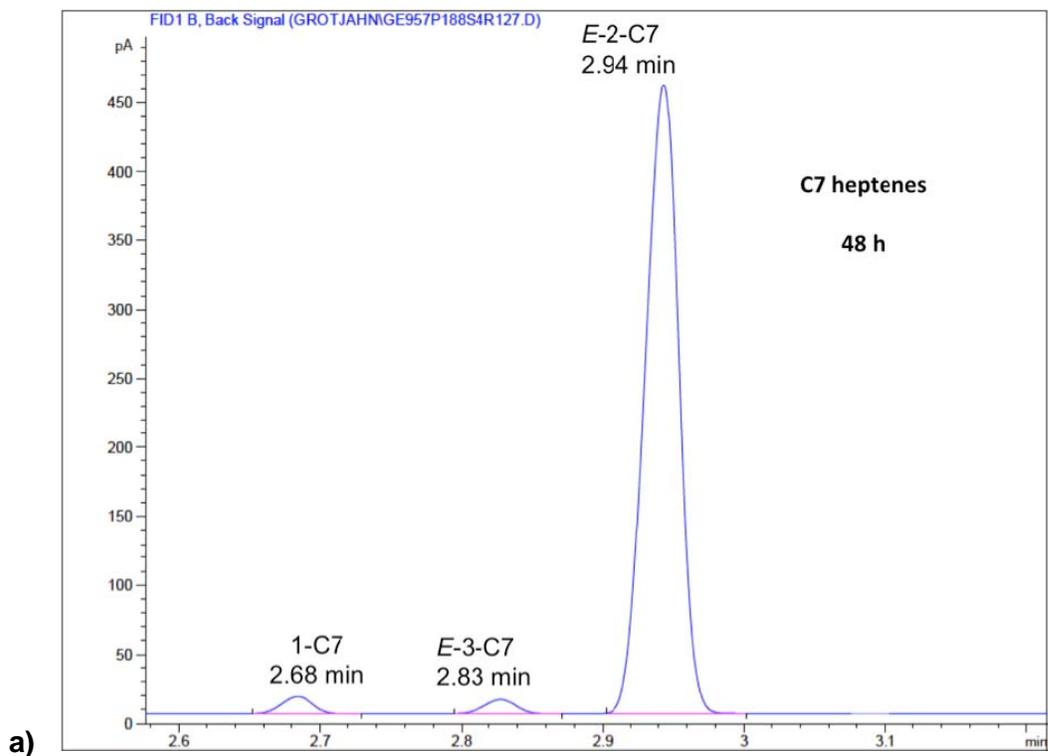
Time	5 h	22 h	48 h	48 h with added Z-2 (1.0 %) and E-3 (1.0 %) ^a
 (2.68 min)	114.62	21.91	18.97	11.99
% starting material remaining ^b	45.5	6.3	2.4	2.4
 (2.94 min)	137.46	319.89	748.84	474.43
% of E-2 ^b	54.5	92.8	95.5	93.4
 (2.83 min)	0	3.08	16.40	15.47
% of E-3 ^b	0	0.9	2.1	3.0
 (3.09 min)	0	0	0	5.93
% of Z-2 ^b	0	0	0	1.2
Total area	252.08	344.88	784.21	507.82

^a Spiked with 0.005 mmol (1.0 %) of Z-2 and 0.005 mmol (1.0 %) of E-3. ^b Calculated by taking the ratios of integrations of the specified retention times.

Scheme S-V-2a. a) Gas chromatography temperature program for C7 reaction mixtures. **b)** Gas chromatogram for authentic C7 mixture of 1-heptene, E-3-heptene, E-2-heptene, and Z-2-heptene respectively.



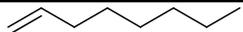
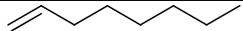
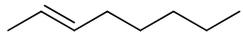
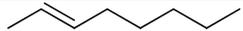
Scheme S-V-2b. Gas chromatogram C7 reaction mixtures **a)** 48 h. **b)** 48 h with added 0.6 mg *Z*-2-heptene (1.0 %) and 0.8 mg *E*-3-heptene (1.0 %).



V-3. Data for manuscript Table 1, entry 3. Procedure for isomerization of 1-octene to *E*-2-octene using 1 mol% catalyst at 40 °C in acetone-*d*₆.

Following the general procedure, 1-octene (56.0 mg, 0.499 mmol) and catalyst **1 + 3** (3.5 mg, 0.005 mmol, 1 mol%) were used. Reaction was conducted at 40 °C using an oil bath. At specified time points, ¹H NMR spectra were obtained and 5 μL of reaction mixture was removed under glovebox atmosphere for GC analysis. For addition of *Z*-2-octene and *E*-3-octene, stock solution of 200 μL was prepared with *Z*-2-octene (11.2 mg, 0.10 mmol) and *E*-3-octene (11.5 mg, 0.10 mmol). 10 μL of this solution was added to the reaction point at 48 h time point.

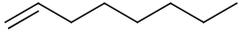
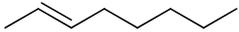
Table S-V-3a. Yields determined by NMR in isomerization of **1-octene**. Measured integrals in arbitrary units and derived percent starting material remaining and product yields.

	Measured integrals in arbitrary units relative to internal standard = 10.0 units and (in bold) derived per cent yields of products and amount of starting 1-alkene				
Time	0 h	5 h	22 h	48 h	48 h with added <i>Z</i> -2 (1.0 %) and <i>E</i> -3 (1.0 %) ^a
 (5.80 ppm)	61.50	28.45	4.85 (4.52)	1.74 (1.83)	1.80 (1.61)
 (4.89 – 4.97 ppm)	124.49	57.41	9.69	3.35	3.56
units per proton ^b	62.00	28.62	3.94	1.70	1.79
% starting material remaining ^c	100	46.2	6.4	2.7	2.9
 (5.42 ppm) ^d	0	66.30	114.85	119.90	121.59
 (1.60 ppm)	0	98.94	170.46	176.87	177.53 ^e
units per proton ^b	0	33.05	57.06	59.35	59.82
% of <i>E</i> -2 ^f	0	53.3	92.0	95.7	96.5
 (0.94 ppm)	0	0	1.44	4.45	6.71
units per proton ^b	0	0	0.48	1.48	2.2
% of <i>E</i> -3 ^f	0	0	0.8	2.4	3.6

^a Spiked with 0.0050 mmol (1.0 %) of *Z*-2 and 0.0051 mmol (1.0 %) of *E*-3. ^b Calculated by taking the average of integrations of the specified resonances. ^c Calculated by dividing units per proton of starting material at time indicated by units per proton value at hour 0. ^d Includes vinylic H for *E*-2, *E*-3 and *Z*-2, but none of these species are present in more than 1% yield until about 24 h, where *E*-3-octene is the most prevalent (2.4 % at 48 h). We note that if one uses only the δ 1.60 ppm resonance value at 48 h, one gets 95.1% yield. ^e Includes integration for *Z*-2 methyls

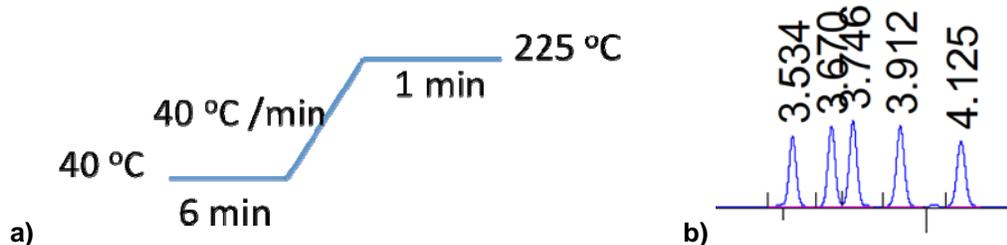
(3H). ^f Calculated by dividing units per proton of product at time indicated by the units per proton value of starting material at hour 0.

Table S-V-3b. Ratios determined by GC in isomerization of **1-octene** using 1 mol% catalyst at 40 °C.

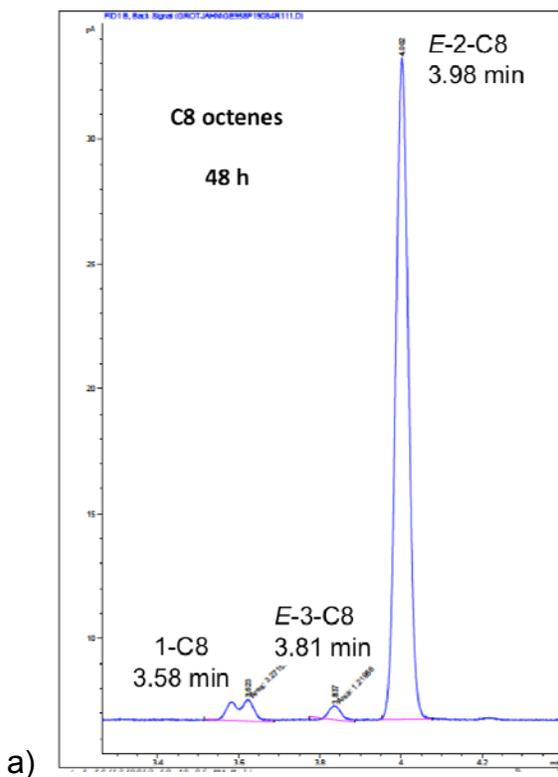
Time	5 h	22 h	48 h	48h with added Z-2 (1.0 %) and E-3 (1.0 %) ^a
 (3.58 min)	262.60	53.90	3.27	16.03
% starting material remaining ^b	46.2	9.3	5.3	4.3
 (3.98 min)	305.74	521.71	56.80	338.75
% of E-2 ^b	53.8	89.6	92.7	92.1
 (3.81 min)	0	6.55	1.22	10.09
% of E-3 ^b	0	1.1	2.0	2.7
 (4.19 min)	0	0	0	2.80
% of Z-2 ^b	0	0	0	0.8
Total	568.34	582.16	61.29	367.67

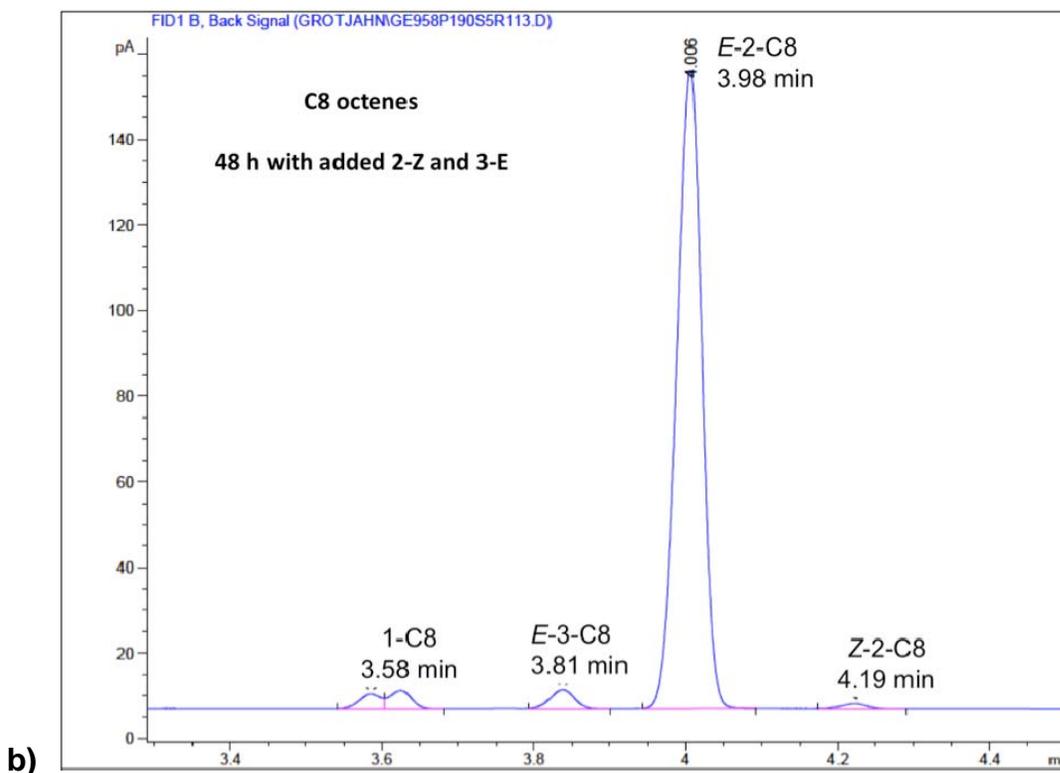
^a Spiked with 0.0050 mmol (1.0 %) of Z-2 and 0.0051 mmol (1.0 %) of E-3. ^b Calculated by taking the ratios of integrations of the specified retention times.

Scheme S-V-3a. A) Gas chromatography temperature program for C8 reaction mixtures. **B)** Gas chromatogram for authentic C8 mixture of 1-octene, *E*-4-octene, *E*-3-octene, *E*-2-octene, and *Z*-2-octene respectively.



Scheme S-V-3b. Gas chromatogram C8 reaction mixtures a) 48 h. b) after addition of *Z*-2-octene (1.0 %) and *E*-3-heptene (1.0 %).

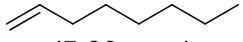
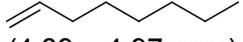
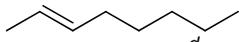
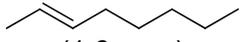




V-4. Data for manuscript Table 1, entry 4. Procedure for isomerization of 1-octene to *E*-2-octene using 1 mol% catalyst in presence of 1 mol% CH₃CN at 40 °C in acetone-*d*₆.

Following the general procedure, 1-octene (56.0 mg, 0.499 mmol) and catalyst **1 + 3** (3.6 mg, 0.005 mmol, 1 mol%) were used. 0.2 μL of a solution prepared with mixing acetone-*d*₆ (200 μL) and acetonitrile (0.8 mg, 0.02 mmol) was added prior to addition of catalyst **1**. Reaction was conducted at 40 °C using an oil bath. At specified time points, ¹H NMR spectra were obtained and 5 μL of the reaction mixture was removed under glovebox atmosphere for GC analysis. For addition of *Z*-2-octene and *E*-3-octene, a stock solution of 200 μL was prepared with *Z*-2-octene (11.1 mg, 0.10 mmol) and *E*-3-octene (11.5 mg, 0.10 mmol). 10 μL of this solution was added to the reaction point at 122 h time point.

Table S-V-4a. Yields determined by NMR in isomerization of **1-octene**. Measured integrals in arbitrary units and derived percent starting material remaining and product yields.

Time	Measured integrals in arbitrary units relative to internal standard = 10.0 units and (in bold) derived per cent yields of products and amount of starting 1-alkene								
	0 h	1 h	5 h	22 h	48 h	72 h	97 h	122 h	122 h with added Z-2 (1.0 %) and E-3 (1.0 %) ^a
 (5.80 ppm)	68.98	63.24	44.70	14.99	4.37	2.54	1.68	1.85	1.72
 (4.89 – 4.97 ppm)	139.93	127.74	90.72	30.47	8.63	5.03	3.91	3.55	3.42
units per proton ^b	69.64	63.66	45.14	15.15	4.33	2.52	1.86	1.80	1.71
% starting material remaining ^c	100	91.4	64.8	21.8	6.2	3.6	2.7	2.6	2.5
 (5.42 ppm) ^d	0	13.89	47.52	107.61	128.84	132.24	132.84	132.02	135.48
 (1.6 ppm)	0	21.01	71.80	162.08	190.92	195.47	196.95	194.51	197.31
units per proton ^b	0	6.98	23.86	53.94	63.95	65.54	65.96	65.31	66.56
% of E-2 ^f	0	10.0	34.3	77.4	91.8	94.1	94.7	93.8	95.6
 (0.94 ppm)	0	0	0	2.42	2.29	4.02	5.58	5.90	8.56
units per proton ^b	0	0	0	0.81	0.76	1.34	1.86	1.97	2.85
% of E-3 ^f	0	0	0	1.2	1.1	1.9	2.7	2.8	4.1

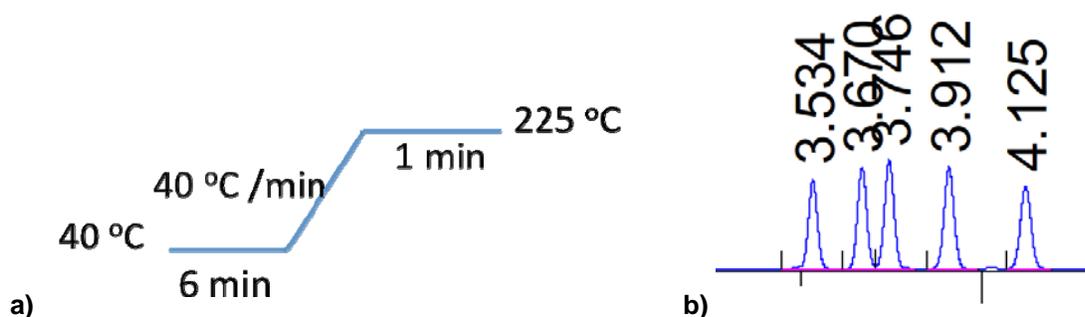
^a Spiked with 0.0050 mmol (1.0 %) of Z-2 and 0.0051 mmol (1.0 %) of E-3. ^b Calculated by taking the average of integrations of the specified resonances. ^c Calculated by dividing units per proton of starting material at time indicated by units per proton value at hour 0. ^d Includes vinylic H for E-2, E-3 and Z-2, but none of these species are present in more than 1% yield until about 24 h, where E-3-octene is the most prevalent (2.8 % at 122 h). We note that if one uses the δ 1.60 ppm resonance value at 122 h, one still gets 93.1% yield, which matches GC results (Table S-V-4b). ^e Includes integration for Z-2 methyls (3H). ^f Calculated by dividing units per proton of product at time indicated by the units per proton value of starting material at hour 0.

Table S-V-4b. Ratios determined by GC in isomerization of **1-octene** using 1 mol% catalyst at 40 °C.

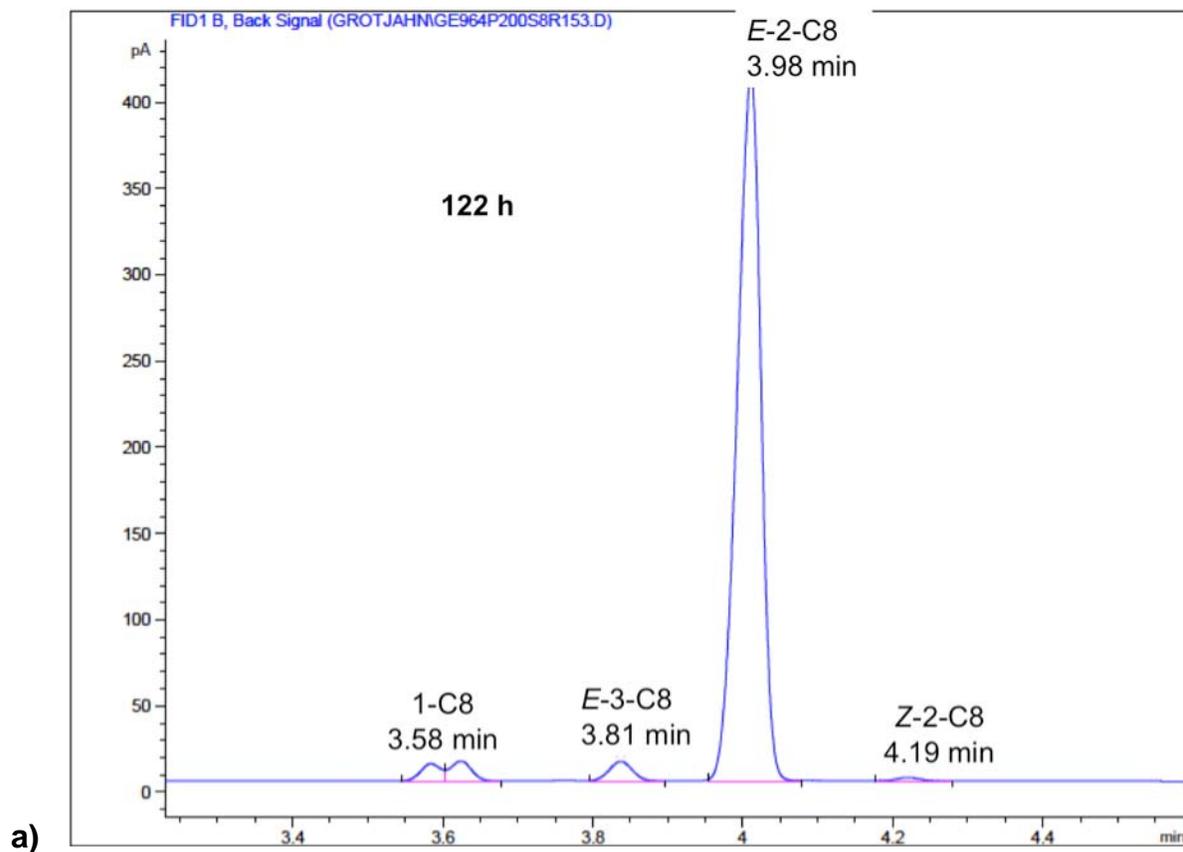
Time	48 h	72 h	97 h	122 h	122 h with added Z-2 (1.0 %) and E-3 (1.0 %) ^a
 (3.58 min)	26.88	62.97	44.56	41.94	39.92
% starting material remaining ^b	7.5	5.3	4.5	4.3	4.2
 (3.98 min)	327.72	1110.65	916.60	903.69	858.69
% of E-2 ^b	91.4	93.0	93.3	93.1	91.4
 (3.81 min)	3.88	19.91	20.90	24.59	31.14
% of E-3 ^b	1.1	1.7	2.1	2.5	3.3
 (4.19 min)	0	0	0	4.31	10.20
% of Z-2 ^b	0	0	0	0	1.1
Total	358.48	1193.53	982.06	970.22	939.95

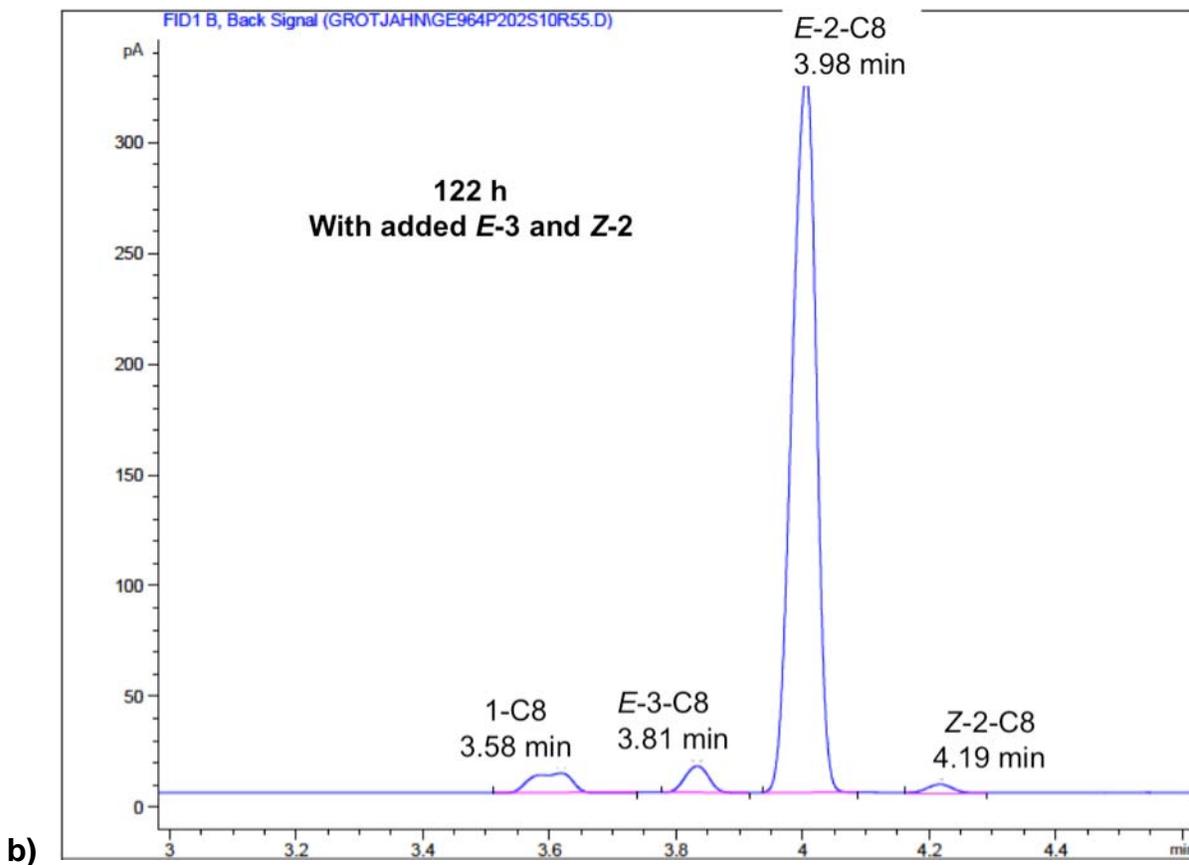
^a Spiked with 0.0050 mmol (1.0 %) of Z-2 and 0.0051 mmol (1.0 %) of E-3. ^b Calculated by taking the ratios of integrations of the specified retention times.

Scheme S-V-4a. A) Gas chromatography temperature program for C8 reaction mixtures. **B)** Gas chromatogram for authentic C8 mixture of 1-octene, E-4-octene, E-3-octene, E-2-octene, and Z-2-octene respectively.



Scheme S-V-4b. Gas chromatogram C8 reaction mixtures a) 48 h. b) after addition of Z-2-octene (1.0 %) and E-3-heptene (1.0 %).

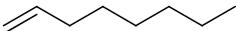
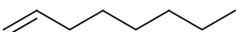
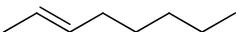
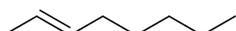




V-5. Data for manuscript Table 1, entry 5. Procedure for isomerization of 1-octene to *E*-2-octene using 1 mol% catalyst prepared *in situ* at 40 °C in acetone- d_6 .

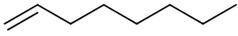
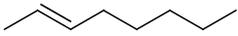
Using a J. Young NMR tube, a solution of 4-(*tert*-butyl)-2-(diisopropylphosphino)-1-methyl-1*H*-imidazole (2.6 mg, 0.01 mmol, 1 mol%) is added to a solution of *tris*(acetonitrile)pentamethylcyclopentadienylruthenium (II) hexafluorophosphate (5.0 mg, 0.01 mmol, 1 mol%) after acquiring an initial spectrum 1-octene (56.9 mg, 0.507 mmol), was added. Reaction was conducted at 40 °C using an oil bath. At specified time points, ^1H NMR spectra were obtained and 5 μL of reaction mixture was removed under glovebox atmosphere for GC analysis. For addition of *Z*-2-octene and *E*-3-octene, stock solution of 200 μL was prepared with *Z*-2-octene (11.1 mg, 0.10 mmol) and *E*-3-octene (11.5 mg, 0.10 mmol). 10 μL of this solution was added to the reaction point at 122 h time point.

Table S-V-5a. Yields determined by NMR in isomerization of **1-octene** by catalyst formed *in situ*. Measured integrals in arbitrary units and derived percent starting material remaining and product yields.

	Measured integrals in arbitrary units relative to internal standard = 10.0 units and (in bold) derived per cent yields of products and amount of starting 1-alkene								
Time	0 h	1 h	5 h	22 h	48 h	72 h	97 h	122 h	122 h with added Z-2 (1.0 %) and E-3 (1.0 %) ^a
 (5.80 ppm)		33.17	27.78	14.14	5.51	2.82	1.54	1.18	1.18
 (4.89 – 4.97 ppm)		67.11	56.28	28.41	11.00	5.78	3.13	2.40	2.34
units per proton ^b	34.58	33.43	28.02	14.18	5.50	2.87	1.56	1.19	1.17
% starting material remaining ^c		96.7	81.0	41.0	15.9	8.3	4.5	3.4	3.4
 (5.42 ppm) ^d	0	3.47	14.25	41.84	59.26	64.51	66.62	67.43	69.02
 (1.60 ppm)	0	5.18	21.49	62.55	88.18	96.81	98.75	100.02	100.70
units per proton ^b	0	1.73	7.15	20.88	29.49	32.26	33.07	33.49	33.94
% of E-2 ^f	0	5.0	20.7	60.4	85.3	93.3	95.6	96.8	98.2
 (0.94 ppm)	0	0	0	0	0.97	2.01	1.82	2.34	3.39
units per proton ^b	0	0	0	0	0.32	0.67	0.61	0.78	1.13
% of E-3 ^f	0	0	0	0	0.9	1.9	1.8	2.2	3.3

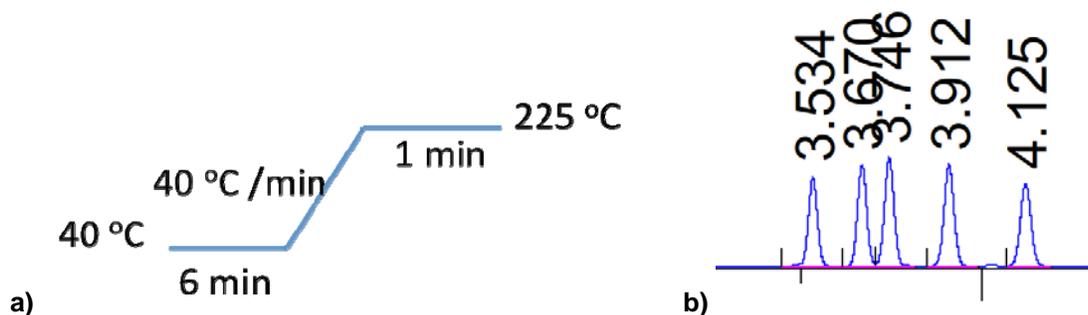
^a Spiked with 0.0050 mmol (1.0 %) of Z-2 and 0.0051 mmol (1.0 %) of E-3. ^b Calculated by taking the average of integrations of the specified resonances. ^c Calculated by dividing units per proton of starting material at time indicated by units per proton value at hour 0. ^d Includes vinylic H for E-2, E-3 and Z-2, but none of these species are present in more than 1% yield until about 24 h, where E-3-octene is the most prevalent (2.2 % at 122 h). We note that if one uses the δ 1.60 ppm resonance value at 122 h, one still gets 96.4% yield. ^e Includes integration for Z-2 methyls (3H). ^f Calculated by dividing units per proton of product at time indicated by the units per proton value of starting material at hour 0.

Table S-V-5b. Ratios determined by GC in isomerization of **1-octene** using 1 mol% catalyst at 40 °C.

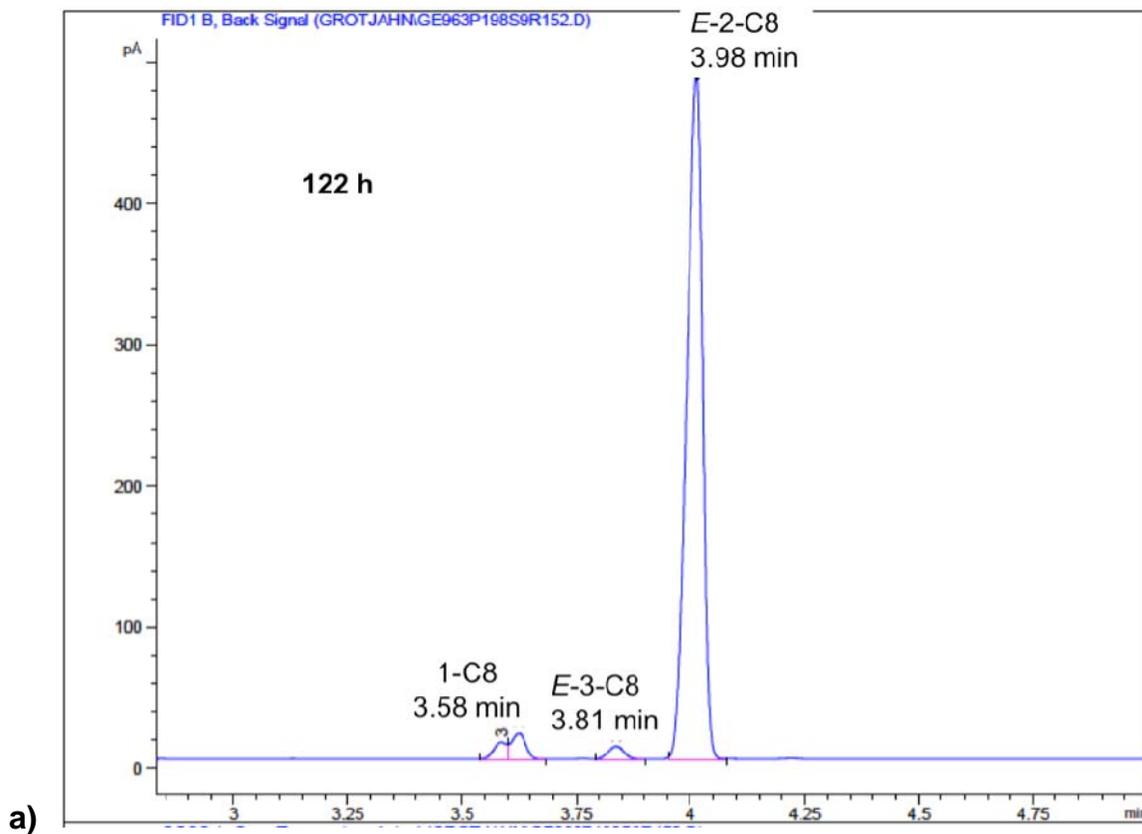
Time	48 h	72 h	97 h	122 h	122 h with added Z-2 (1.0 %) and E-3 (1.0 %) ^a
 (3.58 min)	131.68	109.34	83.94	64.09	57.21
% starting material remaining ^b	16.8	9.5	6.3	5.1	5.0
 (3.98 min)	644.86	1028.44	1223.41	1171.16	1048.01
% of E-2 ^b	82.4	89.4	92.2	93.2	91.6
 (3.81 min)	5.83	12.55	18.80	21.92	30.25
% of E-3 ^b	0.8	1.1	1.4	1.7	2.6
 (4.19 min)	0	0	0	0	9.15
% of Z-2 ^b	0	0	0	0	0.8
Total	782.37	1150.33	1326.15	1257.17	1144.62

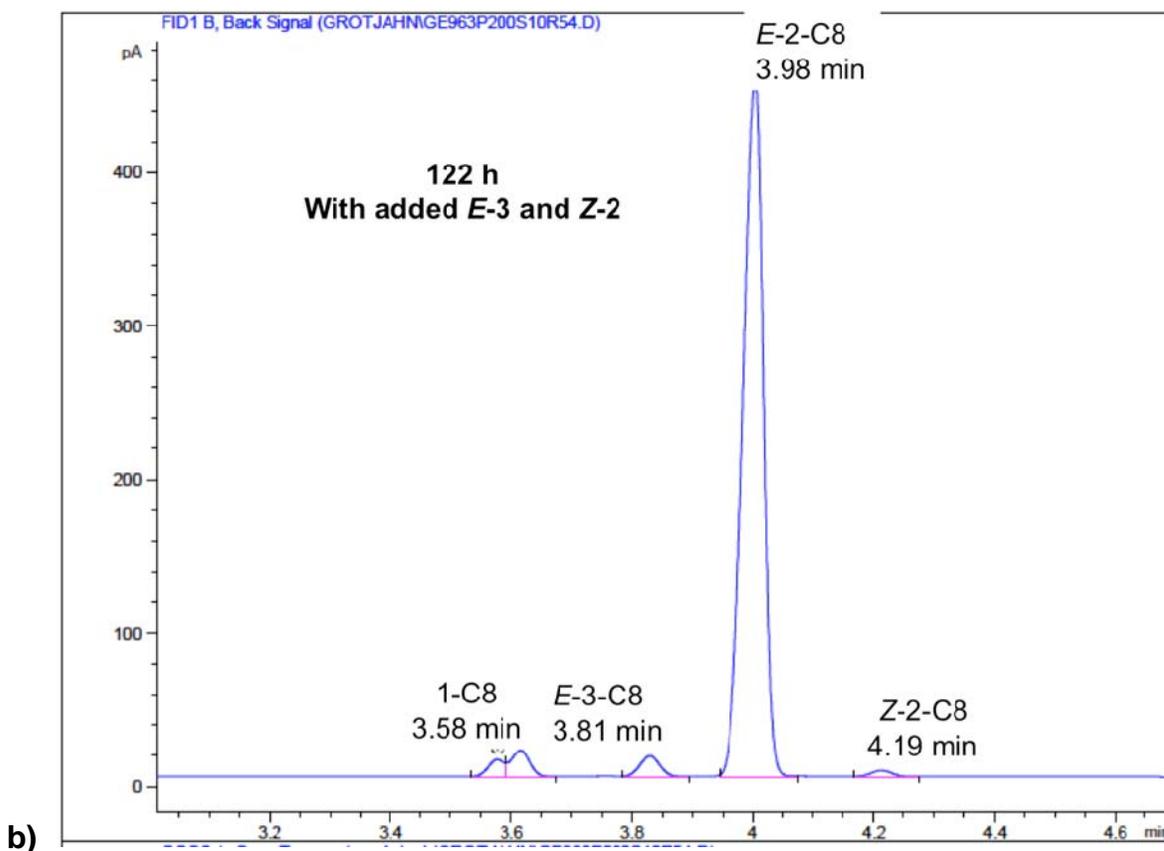
^a Spiked with 0.0050 mmol (1.0 %) of Z-2 and 0.0051 mmol (1.0 %) of E-3. ^b Calculated by taking the ratios of integrations of the specified retention times.

Scheme S-V-5a. **a)** Gas chromatography temperature program for C8 reaction mixtures. **b)** Gas chromatogram for authentic C8 mixture of 1-octene, E-4-octene, E-3-octene, E-2-octene, and Z-2-octene respectively.



Scheme S-V-5b. Gas chromatogram C8 reaction mixtures a) 48 h. b) after addition of Z-2-octene (1.0 %) and E-3-heptene (1.0 %).

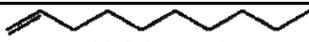


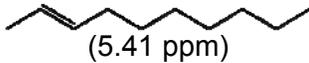
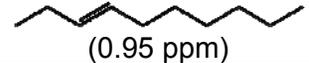


V-6. Data for manuscript Table 1, entry 6. Procedure for isomerization of 1-decene to *E*-2-decene using 2 mol% catalyst at 40 °C in acetone-*d*₆.

Following the general procedure, 1-decene (72.0 mg, 0.513 mmol) and catalyst **1** + **3** (7.1 mg, 0.010 mmol, 2 mol%) were used. Reaction was conducted at 40 °C using an oil bath. At specified time points, ¹H NMR spectra were obtained and 5 μL of reaction mixture was removed under glovebox atmosphere for GC analysis.

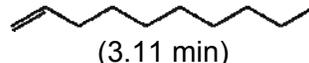
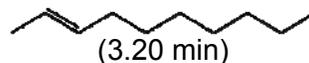
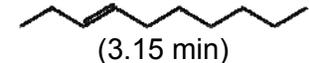
Table S-V-6a. Yields determined by NMR in isomerization of **1-decene** using 1 mol% catalyst at 40 °C.

Time	Measured integrals in arbitrary units relative to internal standard = 10.0 units and (in bold) derived per cent yields of products and amount of starting 1-alkene			
	0 h	5 h	21 h	48 h
 (5.80 ppm)	66.84	30.40	5.18	1.87
 (4.91 ppm)	136.67	60.95	10.46	3.41

units per proton ^a	67.84	30.45	5.21	1.76
% starting material remaining ^b	100	44.9	7.7	2.6
 (5.41 ppm)	0	72.13	123.18	129.93
units per proton ^a	0	36.06	61.59	65.0
% yield of product ^c	0	53.2	90.8	95.8
 (0.95 ppm)	0	0	2.66	4.47
units per proton ^a	0	0	0.89	1.49
% of E-3 ^c	0	0	1.3	2.2

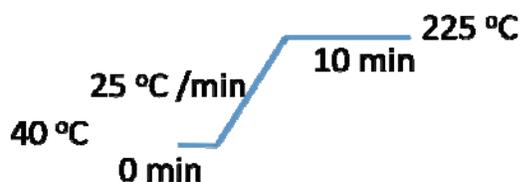
^aCalculated by taking the average of integrations of the specified resonances. ^bCalculated by dividing units per proton of starting material at time indicated by units per proton value at hour 0. ^cCalculated by dividing units per proton of product at time indicated by the units per proton value of starting material at hour 0.

Table S-V-6b. Ratios determined by GC in isomerization of **1-decene** using 1 mol% catalyst at 40 °C.

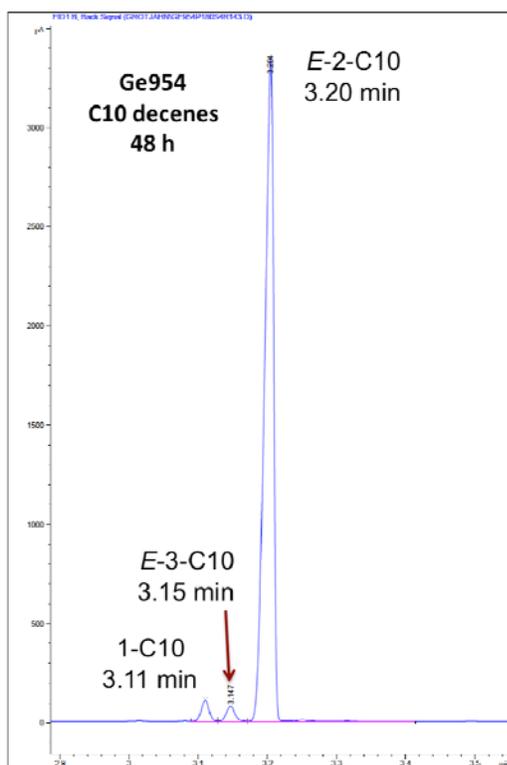
Time	5 h	21 h	48 h
 (3.11 min)	1050.30	258.99	81.44
% starting material remaining ^a	46.4	7.4	2.6
 (3.20 min)	1210.41	3177.41	2499.31
% yield of E-2 ^a	53.5	91.3	95.4
 (3.15 min)	0	0	63.13
% of E-3 ^a	0	0	2.0

^aCalculated by taking the ratios of integrations of the specified retention times

Scheme S-V-6a. Gas chromatography temperature program for C10 reaction mixtures.



Scheme S-V-6b. Gas chromatogram C10 reaction mixtures at 48 h.

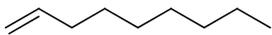
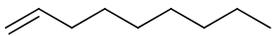
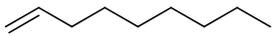
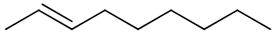
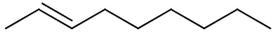


V-7. Manuscript Table 1, footnote i to entry 6: Isomerization of 1-decene using 5 mol% catalyst at room temperature. 1-decene (72.9 mg, 0.520 mmol) and catalyst **1** + **3** (19.9 mg, 0.0262 mmol, 5.0 mol%) were used. The reaction was conducted at room temperature.

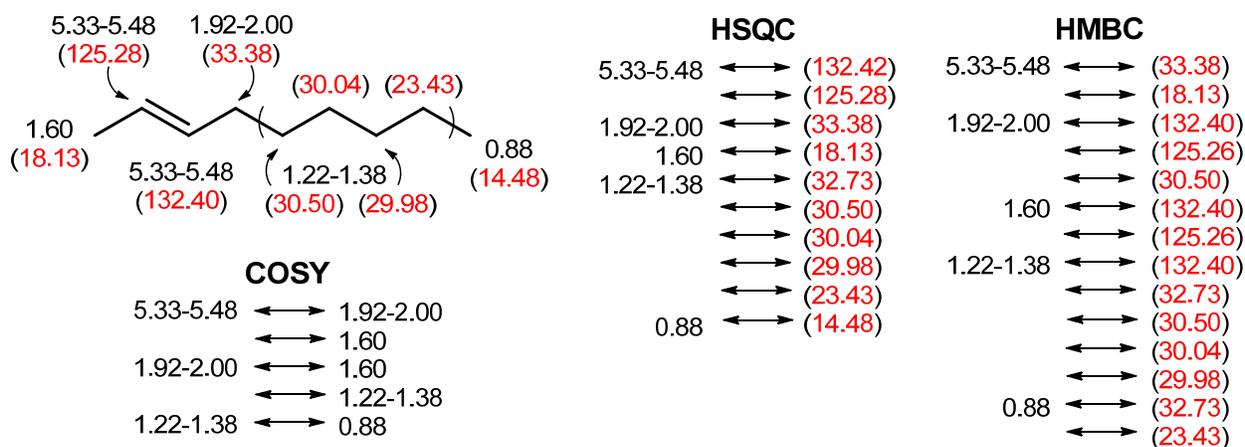
For 1-decene in the mixture: ^1H NMR (500 MHz, acetone- d_6) δ 5.80 (tdd, $J = 7.0, 10.5, 17.0, 1\text{H}$), 4.97 (dtd, $J = 1.5, 2.0, 17.0, 1\text{H}$), 4.89 (tdd, $J = 1.5, 2.0, 10.5, 1\text{H}$), 1.99-2.07 (m, 2H), 1.35-1.43 (m, 2H), 1.22-1.35 (m, 10H), 0.88 ppm (t, $J = 7.0, 3\text{H}$). ^{13}C NMR (125.73 MHz, acetone- d_6) δ 139.88, 114.71, 34.63, 32.77, 30.35, 30.18, 30.02, 29.87, 23.46, 14.48 ppm.

For the (*E*)-2-decene in the mixture: ^1H NMR (500 MHz, acetone- d_6) δ 5.35-5.45 (m, 2H), 1.92-2.00 (m, 2H), 1.60 (~d of narrow m, $J \approx 5, 3\text{H}$), 1.22-1.38 (m, 10H), 0.88 ppm (t, $J = 7.0, 3\text{H}$). ^{13}C NMR (125.73 MHz, acetone- d_6) δ 132.42, 125.28, 33.38, 32.73, 30.50, 30.04, 29.98, 23.43, 18.13, 14.45 ppm.

Table S-V-7a. Isomerization of 1-decene using 5 mol% catalyst **1** at room temperature.

	Measured integrals in arbitrary units relative to internal standard = 10.0 units and (in bold) derived per cent yields of products and amount of starting 1-alkene					
Time	0 h	26 h	50 h	74 h	97 h	121 h
 (5.80 ppm)	78.01	26.88	13.63	7.77	4.73	3.39
 (4.97 ppm)	78.32	27.28	13.77	7.99	4.40	3.47
 (4.89 ppm)	78.85	26.79	13.62	7.84	4.41	3.36
units per proton ^a	78.39	26.98	13.67	7.87	4.51	3.41
% starting material remaining ^b	100	34.4	17.4	10.0	5.7	4.3
 (5.35-5.45 ppm)	0	103.27	129.30	142.53	145.91	150.29
 (1.60 ppm)	0	163.29	200.41	215.49	219.71	227.84
units per proton ^a	0	53.31	65.94	71.60	73.12	75.63
% yield of product ^c	0	68.0	84.1	91.3	93.3	96.5

^aCalculated by taking the average of integrations of the specified resonances. ^bCalculated by dividing units per proton of starting material at time indicated by units per proton value at hour 0. ^cCalculated by dividing units per proton of product at time indicated by the units per proton value of starting material at hour 0.



VI. Manuscript Table 1: Data for control experiments showing differences between Cp*Ru and CpRu catalysts 1 + 3 and 2a

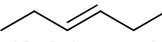
VI-1a. Data for manuscript Table 1, entry 1a. Isomerization of 1-hexene with CpRu catalyst 2a. Following the general procedure, 1-hexene (44.3 mg, 0.526 mmol) and catalyst **2a** (2.2 mg, 0.0036 mmol, 0.7 mol%) were used. The reaction was conducted at room temperature.

For 1-hexene in the mixture: ^1H NMR (500 MHz, acetone- d_6) δ 5.79 (tdd, $J = 5.5, 10.5, 17.5$, 1H), 4.85-5.01 (m, 2H), 2.04 (td, $J = 6.5, 7.0$, 2H), 1.27-1.40 (m, 4H), 0.89 ppm (t, $J = 7.5$, 3H). ^{13}C NMR (125.73 MHz, acetone- d_6) δ 139.88, 114.71, 34.28, 32.04, 22.92, 14.26 ppm.

For the (*E*)-2-hexene in the mixture: ^1H NMR (500 MHz, acetone- d_6) δ 5.35-5.46 (m, 2H), 1.89-1.96 (m, 2H), 1.60 (dd, $J = 1.0, 3.5$, 3H), 1.34 (qt, $J = 7.5, 7.5$, 2H), 0.87 ppm (t, $J = 7.5$, 3H). ^{13}C NMR (125.73 MHz, acetone- d_6) δ 132.15, 125.51, 35.48, 23.48, 18.10, 13.97 ppm.

Table S-VI-1a. Isomerization of 1-hexene using 0.7 mol% CpRu catalyst **2a** at room temperature.

	Measured integrals in arbitrary units relative to internal standard = 10.0 units and (in bold) derived per cent yields of products and amount of starting 1-alkene			
Time	0 h	2 h	146 h	336 h
 (5.79 ppm)	60.64	0.78	0.52	trace
 (4.85-5.01 ppm)	121.06	2.12	1.66	trace
units per proton ^a	60.57	0.97	0.72	trace
% starting material remaining ^b	100	1.6	1.2	trace
 (1.60 ppm)	0	137.24	120.14	110.36
units per proton ^a	0	45.75	40.05	36.79
% yield of product ^c	0	75.5	66.1	60.7
 (1.57 ppm)	0	0	18.06	26.47

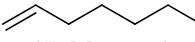
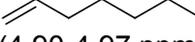
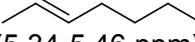
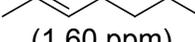
units per proton ^a	0	0	6.02	8.82
% yield of product ^c	0	0	9.9	14.6
 (0.94 ppm)	0	87.83	85.79	82.82
Units per proton ^a	0	14.68	14.30	13.80
% yield of isomer ^c	0	24.2	23.6	22.8

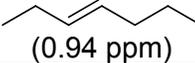
^aCalculated by taking the average of integrations of the specified resonances. ^bCalculated by dividing units per proton of starting material at time indicated by units per proton value at hour 0.

^cCalculated by dividing units per proton of product at time indicated by the units per proton value of starting material at hour 0.

VI-2a. Data for manuscript Table 1, entry 2a. Isomerization of 1-heptene with CpRu catalyst 2a. Following the general procedure, 1-heptene (49.4 mg, 0.503 mmol) and catalyst **2a** (3.0 mg, 0.0050 mmol, 1 mol%) were used. Reaction was conducted at ambient temperature. At specified time points, ¹H NMR spectra were obtained.

Table S-VI-2a. Yields determined by NMR in isomerization of **1-heptene** using 1 mol% CpRu catalyst **2a** at ambient temperature.

Time	Measured integrals in arbitrary units relative to internal standard = 10.0 units and (in bold) derived per cent yields of products and amount of starting 1-alkene		
	0	10 min	4 h
 (5.80 ppm)	83.29	1.08	0.86
 (4.90-4.97 ppm)	169.58	1.86	1.44
units per proton ^a	84.29	0.89	0.77
% starting material remaining ^b	100	1.2	0.9
 (5.34-5.46 ppm) ^c	0	166.58	164.58
 (1.60 ppm)	0	151.43	131.19
units per proton ^a	0	50.48	43.73
% of <i>E</i> -2 ^f	0	59.9	51.9

 (0.94 ppm)	0	96.74	114.19
units per proton ^a	0	32.25	38.06
% of <i>E</i> -3 ^d	0	38.3	45.2

^a Calculated by taking the average of integrations of the specified resonances. ^b Calculated by dividing units per proton of starting material at time indicated by units per proton value at hour 0. ^c Includes vinylic H for *E*-2, *E*-3 and *Z*-2, not used in determination of percentages. ^d Calculated by dividing units per proton of product at time indicated by the units per proton value of starting material at hour 0.

VII. Manuscript Table 1: Data for entries 2e and 2f, control experiments with complexes lacking N-heterocyclic phosphine ligand

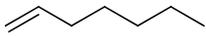
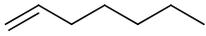
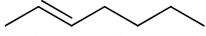
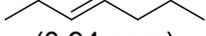
See page S45 below for comparison of rates for entries 2e and 2f with rate of entry 2.

VII-1. Data for manuscript Table 1, entry 2e. Procedure for isomerization of 1-heptene using 4 mol% [Cp*Ru(CH₃CN)₂(P*i*Pr₃)]PF₆ at 40 °C in acetone-*d*₆.

Catalyst [Cp*Ru(CH₃CN)₂(P*i*Pr₃)]PF₆ was prepared by adding an acetone solution of triisopropylphosphine (3.1 mg, 0.0193 mmol, 3.9 mol%) to an acetone solution of [Cp*Ru(CH₃CN)₃]PF₆ (10.4 mg, 0.0206 mmol, 4.1 mol%). After standing overnight at RT, volatiles were removed. Analogous CpRu complexes have been reported.¹ Following the general procedure, 1-heptene (49.1 mg, 0.50 mmol) and internal standard in acetone-*d*₆ were treated with an acetone-*d*₆ solution of the [Cp*Ru(CH₃CN)₂(P*i*Pr₃)]PF₆. Reaction was conducted at 40 °C using an oil bath. At specified time points, ¹H NMR spectra were obtained and 5 μL of reaction mixture was removed under glovebox atmosphere for GC analysis. For addition of *Z*-2-heptene and *E*-3-heptene, stock solution of 200 μL was prepared with *Z*-2-heptene (9.8 mg, 0.10 mmol) and *E*-2-heptene (9.8 mg, 0.010 mmol) and *E*-3-heptene (9.4 mg, 0.099 mmol). 10 μL of this solution was added to the reaction point at 216 h time point.

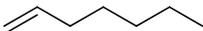
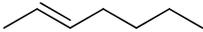
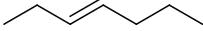
Table S-VII-1a. Yields determined by NMR in isomerization of 1-heptene using 4 mol% catalyst [Cp*Ru(CH₃CN)₂(P*i*Pr₃)]PF₆ at 40 °C.

	Measured integrals in arbitrary units relative to internal standard = 10.0 units and (in bold) derived per cent yields of products and amount of starting 1-alkene.					
Time	0 h	5 h	22 h	72 h	216 h	216 h with added <i>Z</i>-2 (1.0 %) and <i>E</i>-3 (1.0 %) ^a

 (5.80 ppm)	40.00	39.91	39.44	39.34	38.49	38.41
 (4.90-4.97 ppm)	81.32	80.79	80.13	79.39	78.08	78.12
units per proton ^b	40.44	40.23	39.86	39.58	38.86	38.84
% starting material remaining^c	100	99.5	98.6	97.9	96.1	96.0
 (5.34-5.46 ppm) ^d	-	0.1	0.3	0.6	0.9	3.6
units per proton ^b	-	.05	0.15	0.3	0.5	1.8
% of E-2^e	-	0.1	0.4	0.7	1.2	4.4
 (0.94 ppm)	-	-	-	-	-	0.2
units per proton ^b	-	-	-	-	-	0.07
% of E-3^e	-	-	-	-	-	0.2

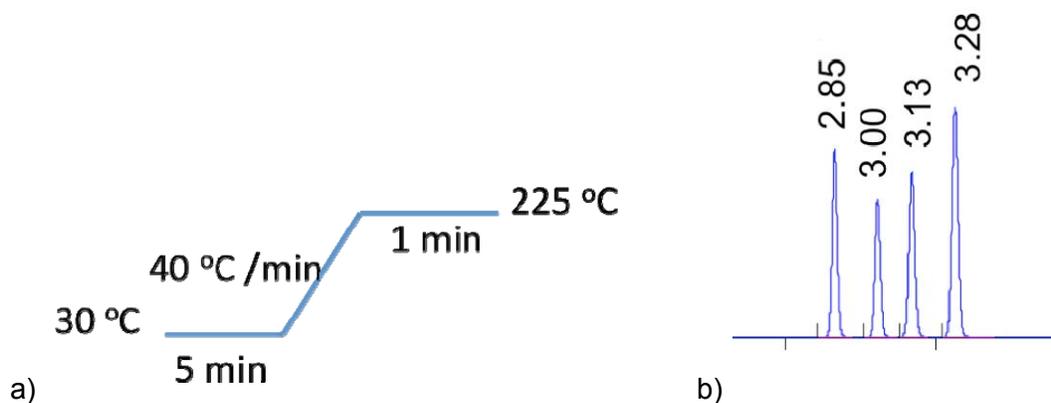
^a Spiked with 0.005 mmol (1.0 %) of Z-2, 0.005 mmol (1.0 %) of E-2, and 0.0050 mmol (1.0 %) of E-3. ^b Calculated by taking the average of integrations of the specified resonances. ^c Calculated by dividing units per proton of starting material at time indicated by units per proton value at hour 0. ^d Includes vinylic H for E-2, E-3 and Z-2, but none of these species are present in more than 1% yield until 216 h. ^e Calculated by dividing units per proton of product at time indicated by the units per proton value of starting material at hour 0.

Table S-VII-1b. Ratios determined by GC in isomerization of **1-heptene** using 4 mol% catalyst at 40 °C.

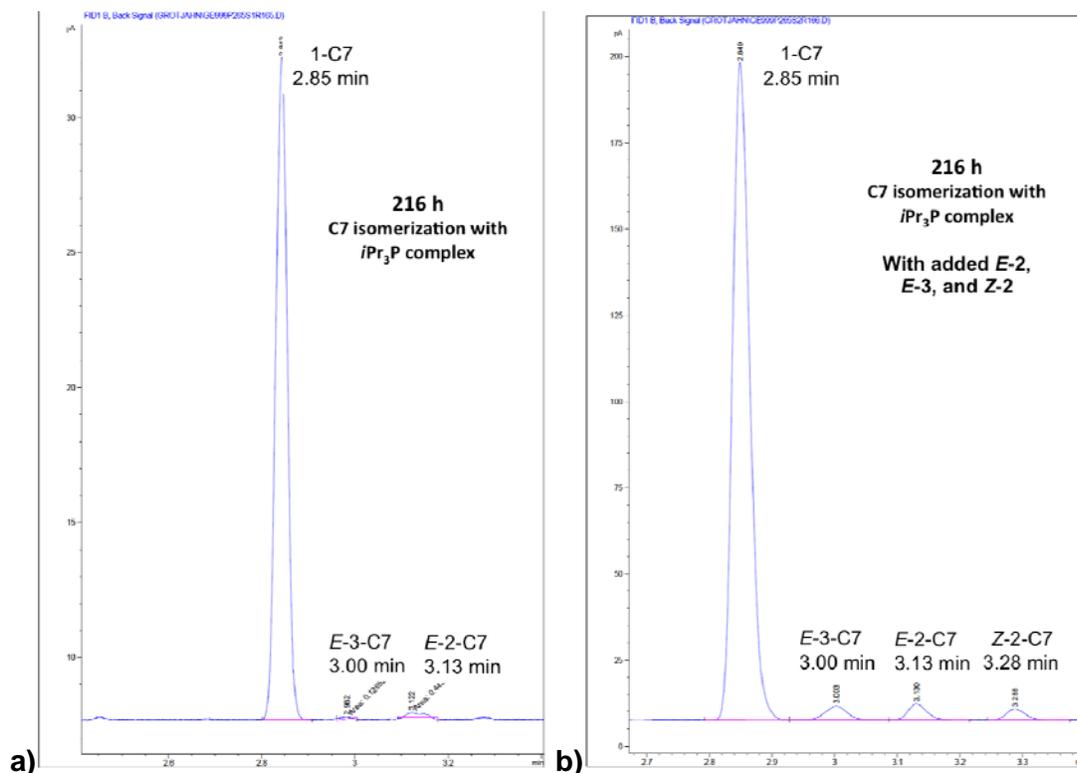
Time	216 h	216 h with added Z-2 (1.0 %) and E-3 (1.0 %) ^a
 (2.85 min)	42.26	363.36
% starting material remaining ^b	98.7	93.2
 (3.13 min)	0.44	10.00
% of E-2 ^b	1.0	2.6
 (3.00 min)	0.13	9.68
% of E-3 ^b	0.2	2.5
 (3.28 min)	-	6.70
% of Z-2 ^b	-	1.7
Total area	42.83	389.74

^a Spiked with 0.005 mmol (1.0 %) of Z-, 0.005 mmol (1.0 %) of E-2, and 0.005 mmol (1.0 %) of E-3. ^b Calculated by taking the ratios of integrations of the specified retention times.

Scheme S-VII-1a. a) Gas chromatography temperature program for C7 reaction mixtures. **b)** Gas chromatogram for authentic C7 mixture of 1-heptene, E-3-heptene, E-2-heptene, and Z-2-heptene respectively. GC runs were performed on a different Agilent 7820A instrument than the one used for other sections of Supporting Information, but equipped with HP-5 column, and under identical conditions. All retention times were observed to be +0.17 min from those using the other instrument.



Scheme S-VII-1b. Gas chromatogram C7 reaction mixtures **a)** 216 h. **b)** 216 h with added *Z*-2-heptene (1.0 %), *E*-2-heptene (1.0 %), and *E*-3-heptene (1.0 %).



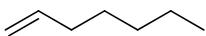
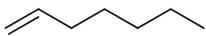
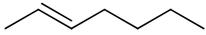
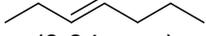
VII-2. Data for manuscript Table 1, entry 2f. Procedure for isomerization of 1-heptene using 4 mol% (initial loading, see note below) [Cp*Ru(CH₃CN)₂(P*i*Pr₂Ph)]PF₆ at 40 °C in acetone-*d*₆.

Catalyst [Cp*Ru(CH₃CN)₂(P*i*Pr₂Ph)]PF₆ was prepared by adding an acetone solution of diisopropylphenylphosphine (4.6 mg, 0.024 mmol, 4 mol%) to an acetone solution of [Cp*Ru(CH₃CN)₃]PF₆ (12.2 mg, 0.024 mmol, 4 mol%). After standing 16.7 h at RT, volatiles were removed. Analogous CpRu complexes have been reported.¹ Following the general procedure, 1-heptene (49.5 mg, 0.504 mmol) and internal standard in acetone-*d*₆ were treated with an acetone-*d*₆ solution of the [Cp*Ru(CH₃CN)₂(P*i*Pr₂Ph)]PF₆. Reaction was conducted at 40 °C using an oil bath. At specified time points, ¹H NMR spectra were obtained and 5 μL of reaction mixture was removed under glovebox atmosphere for GC analysis. For addition of *Z*-2-heptene and *E*-3-heptene, stock solution of 200 μL was prepared with *Z*-2-heptene (9.8 mg, 0.10 mmol) and *E*-2-heptene (9.8 mg, 0.010 mmol) and *E*-3-heptene (9.4 mg, 0.099 mmol). 10 μL of this solution was added to the reaction point at the 312 h time point.

Note about evolution of the catalyst: Over the course of the isomerization reaction, the Cp*Ru fragment migrated from P (³¹P NMR signal at 46.8 ppm) to the arene on P

(³¹P NMR signal at 5.9 ppm). At 2 h reaction time, the P-bound complex vs. Ph-bound complex ratio was 2.1 to 1.0 as determined by the ¹H NMR signals at 7.65-7.42 ppm (unmetallated Ph) and 6.08-6.01 ppm (Cp**Ru*-bound Ph), respectively. This ratio became 1.0 to 1.2 at 168 h and 1.0 to 1.4 at 312 h.

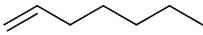
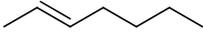
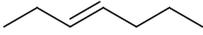
Table S-VII-2a. Yields determined by NMR in isomerization of **1-heptene** using 4 mol% catalyst (initial loading, see note) [*Cp***Ru*(CH₃CN)₂(*P*/*i*Pr₂Ph)]PF₆ at 40 °C.

	Measured integrals in arbitrary units relative to internal standard = 10.0 units and (in bold) derived per cent yields of products and amount of starting 1-alkene.							
Time	0 h	2 h	22 h	48 h	72 h	168 h	312 h	312 h with added Z-2 (1.0 %) and E-3 (1.0 %) ^a
 (5.80 ppm)	52.33	53.34	51.99	51.63	51.96	51.71	51.92	51.94
 (4.90-4.97 ppm)	106.64	108.65	105.16	105.07	105.44	104.16	105.03	104.95
units per proton ^b	52.99	54.00	52.38	52.23	52.47	51.96	52.32	52.30
% starting material remaining ^c	100	101.9	98.8	98.6	99.0	98.1	98.7	98.7
 (5.34-5.46 ppm) ^d	-	-	-	0.2	0.2	0.3	0.5	4.0
units per proton ^b	-	-	-	0.1	0.1	0.1	0.2	2.0
% of E-2 ^e	-	-	-	0.2	0.2	0.2	0.4	3.8
 (0.94 ppm)	-	-	-	-	-	-	-	0.3
units per proton ^b	-	-	-	-	-	-	-	0.1
% of E-3 ^e	-	-	-	-	-	-	-	0.2

^a Spiked with 0.005 mmol (1.0 %) of Z-2, 0.005 mmol (1.0 %) of E-2, and 0.0050 mmol (1.0 %) of E-3. ^b Calculated by taking the average of integrations of the specified resonances. ^c Calculated by dividing units per proton of starting material at time indicated by units per proton value at hour 0. ^d Includes vinylic H for E-2, E-3 and Z-2, but none of these species are present

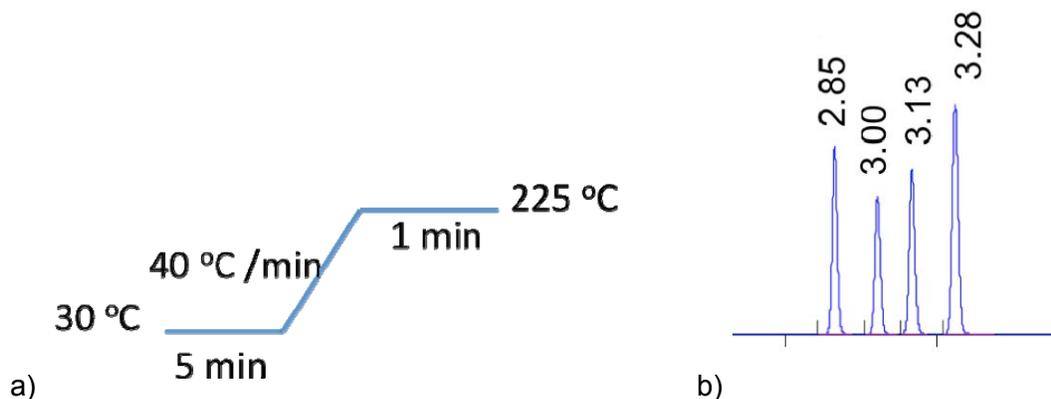
in more than 1% yield until about 312 h. ^e Calculated by dividing units per proton of product at time indicated by the units per proton value of starting material at hour 0.

Table S-VII-2b. Ratios determined by GC in isomerization of **1-heptene** using 4 mol% catalyst (initial loading, see note on page S38) at 40 °C.

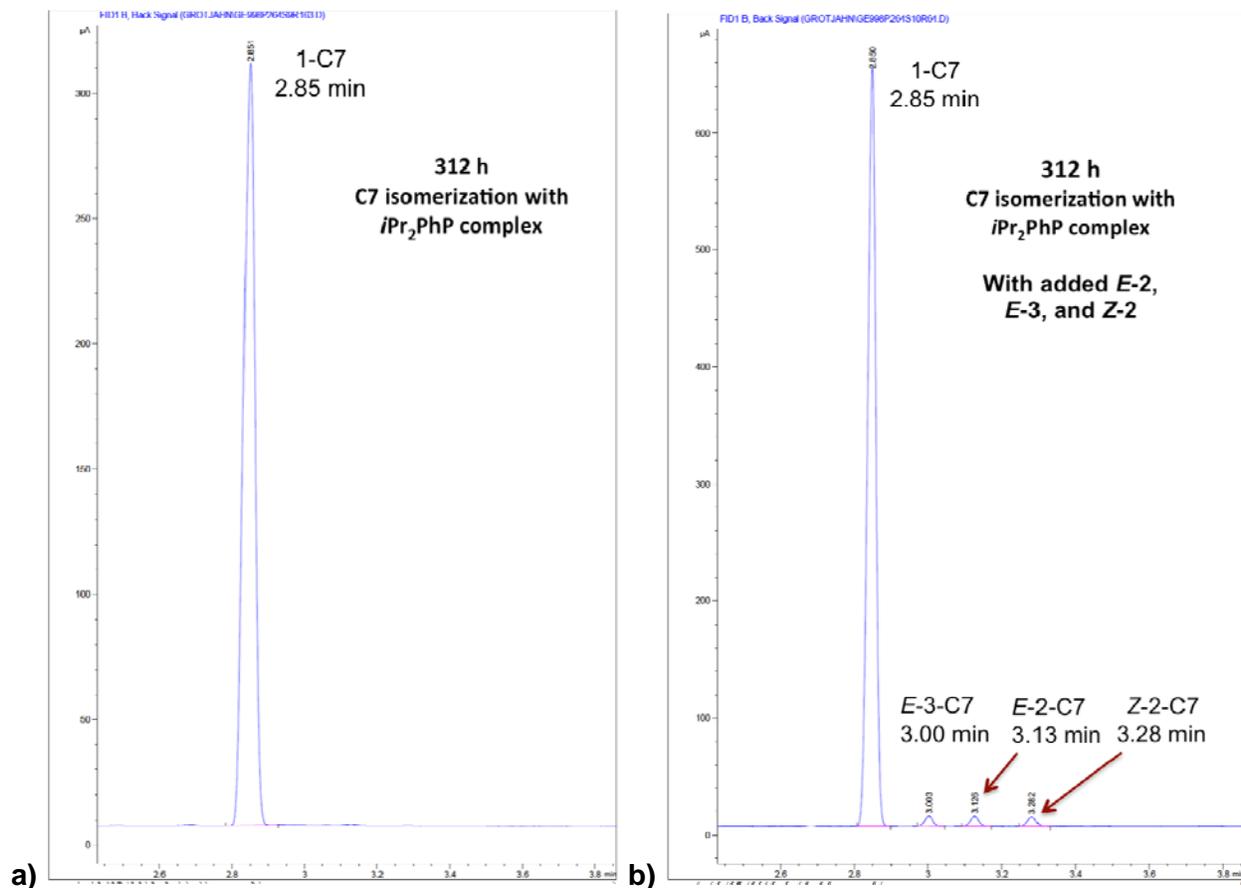
Time	312 h	312 h with added Z-2 (1.0 %) and E-3 (1.0 %) ^a
 (2.85 min)	648.16	1009.76
% starting material remaining ^b	100	96.4
 (3.13 min)	0	12.44
% of E-2 ^b	0	1.2
 (3.00 min)	0	12.99
% of E-3 ^b	0	1.2
 (3.28 min)	0	12.80
% of Z-2 ^b	0	1.2
Total area	648.16	1047.99

^a Spiked with 0.005 mmol (1.0 %) of Z-2 and 0.005 mmol (1.0 %) of E-3. ^b Calculated by taking the ratios of integrations of the specified retention times.

Scheme S-VII-2a. a) GC temperature program for C7 reaction mixtures. **b)** Gas chromatogram for authentic C7 mixture of 1- heptene, E-3-heptene, E-2-heptene, and Z-2-heptene respectively. GC runs were performed on a different Agilent 7820A instrument than the one used for other sections of SI, but otherwise under identical conditions. All retention times were observed to be +0.17 min from those using the other instrument.



Scheme S-VII-2b. Gas chromatogram C7 reaction mixtures **a)** 312 h. **b)** 312 h with added *Z*-2-heptene (1.0 %), *E*-2-heptene (1.0 %), and *E*-3-heptene (1.0 %).



Rate comparison between entries 2, 2e, and 2f

For entry 2 (isomerization of 1-heptene using 1 mol% **1** + **3**)

At 22 h, 93.3% yield of (*E*)-2-heptene = 4.24 h⁻¹

For entry 2e (isomerization using 4 mol% of the P*i*Pr₃ complex)

At 216 h, 1.2% yield of (*E*)-2-heptene = 0.0014 h⁻¹

Ratio of rates = 4.24 / 0.0014 = 3029 to 1.

For entry 2f, the evolution of the catalyst to a coordinatively saturated arene-bound species (presumed to be catalytically inactive) complicates the analysis. However, given that the observed ratio of P-bound to arene-bound species had reached 1.0 to 1.2 at 168 h, we estimate rate as follows. Assume conservatively that only one half of added catalyst was still active over the **entire** 168 h. Then catalyst loading would be 2 mol%, giving at 168 h a TOF = (0.2% product / 2% catalyst)/168 h = 0.0006 h⁻¹. Ratio of rates = 4.24 / 0.0006 = 7067 to 1. We use the 3000 to 1 value in the manuscript as a lower bound.

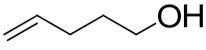
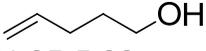
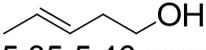
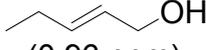
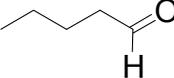
VIII. Manuscript Table 2: Data

VIII-1. Data for manuscript Table 2, entry 1: Isomerization of pent-4-en-1-ol at 40 °C. Following the general procedure, pent-4-en-1-ol (44.2 mg, 0.513 mmol) and catalyst **1** + **3** (3.6 mg, 0.0052 mmol, 1 mol%) were used. The reaction was conducted at 40 °C.

For the pent-4-en-1-ol in the mixture: ¹H NMR (500 MHz, acetone-*d*₆) δ 5.84 (tdd, *J* = 7.5, 10.0, 17.0, 1H), 4.85-5.08 (m, 2H), 3.51-3.59 (m, 2H), 3.47-3.53 (m, 1H), 2.07-2.15 (m, 2H), 1.58 ppm (td, *J* = 7.0, 7.0, 2H).

For the (*E*)-pent-3-en-1-ol in the mixture: ¹H NMR (500 MHz, acetone-*d*₆) δ 5.39-5.52 (m, 2H), 3.47-3.45 (m, 2H), 3.43 (t, *J* = 5.0, 1H), 2.13-2.21 (m, 2H), 1.62 ppm (dd, *J* = 1.0, 5.0, 3H). ¹³C NMR (125.73 MHz, acetone-*d*₆) δ 129.12, 127.17, 62.67, 37.21, 18.21 ppm.

Table S-VIII-1. Isomerization of 4-penten-1-ol using 1 mol% catalyst at 40 °C.

	Measured integrals in arbitrary units relative to internal standard = 10.0 units and (in bold) derived per cent yields of products and amount of starting 1-alkene					
Time	0 h	1 h	2 h	5 h	24 h	46 h
 (5.84 ppm)	63.26	43.21	29.64	10.69	1.52	1.67
 (4.85-5.08 ppm)	129.59	90.35	60.95	21.92	3.60	3.25
units per proton ^a	64.28	44.52	30.20	10.87	1.71	1.64
% starting material remaining ^b	100	69.3	47.0	16.9	2.7	2.5
 (5.35-5.46 ppm)	0	38.11	65.39	104.99	121.34	120.05
units per proton ^a	0	19.06	32.70	52.50	60.67	60.25
% yield of product ^c	0	29.6	50.9	81.7	94.4	93.7
 (0.96 ppm)	0	0	0	0	0	2.34
units per proton ^a	0	0	0	0	0	0.78
% yield of isomer ^c	0	0	0	0	0	1.2
 (9.72 ppm)	0	0	0	0	0	0.43
units per proton ^a	0	0	0	0	0	0.43
% yield of aldehyde ^c	0	0	0	0	0	0.7

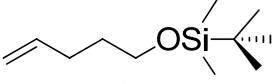
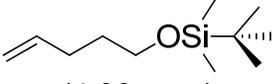
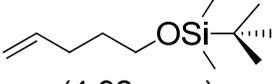
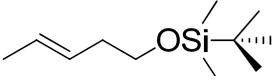
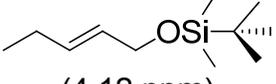
^aCalculated by taking the average of integrations of the specified resonances. ^bCalculated by dividing units per proton of starting material at time indicated by units per proton value at hour 0. ^cCalculated by dividing units per proton of product at time indicated by the units per proton value of starting material at hour 0.

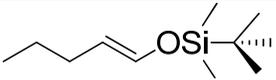
VIII-2. Data for manuscript Table 2, entry 2a: Isomerization of pent-4-en-1-ol *tert*-butyldimethylsilyl ether at 40 °C. Following the general procedure, pent-4-en-1-ol *tert*-butyldimethylsilyl ether (97.5 mg, 0.487 mmol) and catalyst **1** + **3** (3.7 mg, 0.0053 mmol, 1 mol%) were used. The reaction was conducted at 40 °C.

For the pent-4-en-1-ol *tert*-butyldimethylsilyl ether in the mixture: ^1H NMR (500 MHz, acetone- d_6) δ 5.82 (tdd, $J = 6.5, 10.5, 17.5$, 1H), 4.99 (tdd, $J = 2.0, 2.0, 17.5$, 1H), 4.92 (tdd, $J = 1.0, 2.0, 10.5$, 1H), 3.63 (t, $J = 6.5$, 2H), 2.07-2.15 (m, 2H), 1.59 (td, $J = 6.5, 6.5$, 2H), 0.90 (s, 9H), 0.046 ppm (s, 6H).

For the (*E*)-pent-3-en-1-ol *tert*-butyldimethylsilyl ether in the mixture: ^1H NMR (500 MHz, acetone- d_6) δ 5.38-5.52 (m, 2H), 3.61 (t, $J = 6.5$, 2H), 2.13-2.20 (m, 2H), 1.59-1.65 (md, $J = 4.5$, 3H), 0.89 (s, 9H), 0.04 ppm (s, 6H). ^{13}C NMR (125.73 MHz, acetone- d_6) δ 128.85, 127.32, 63.90, 37.15, 26.39, 26.20, 18.92, 18.25, -4.99 ppm.

Table S-VIII-2a. Isomerization of pent-4-en-1-ol *tert*-butyldimethylsilylether at 40 °C.

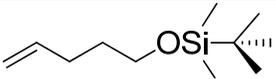
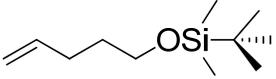
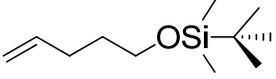
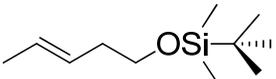
Time	Measured integrals in arbitrary units relative to internal standard = 10.0 units and (in bold) derived per cent yields of products and amount of starting 1-alkene						
	0 h	1 h	2 h	5 h	23 h	45 h	48 h
 (5.82 ppm)	24.42	21.15	18.38	13.21	3.56	1.34	1.16
 (4.99 ppm)	24.66	21.17	18.25	13.29	3.51	1.26	1.18
 (4.92 ppm)	24.79	21.32	18.42	13.40	3.49	1.23	1.14
units per proton ^a	24.62	21.21	18.35	13.30	3.52	1.28	1.16
% starting material remaining ^b	100	86.2	74.5	54.0	14.3	5.2	4.7
 (5.38-5.52 ppm)	0	6.97	12.16	22.84	41.95	46.07	46.83
units per proton ^a	0	3.49	6.08	11.42	20.98	23.04	23.42
% yield of product ^c	0	14.2	24.7	46.4	85.2	93.6	95.1
 (4.12 ppm)	0	0	0	0	0	0	0
units per proton ^a	0	0	0	0	0	0	0
% yield of isomer ^c	0	0	0	0	0	0	0

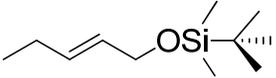
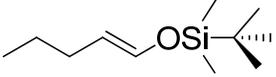
	0	0	0	0	0	0	0
units per proton ^a	0	0	0	0	0	0	0
% yield of silyl enol ether ^c	0						

^aCalculated by taking the average of integrations of the specified resonances. ^bCalculated by dividing units per proton of starting material at time indicated by units per proton value at hour 0. ^cCalculated by dividing units per proton of product at time indicated by the units per proton value of starting material at hour 0.

VIII-2b. Data for manuscript Table 2, entry 2b: Isomerization of pent-4-en-1-ol *tert*-butyldimethylsilyl ether at 70 °C. Following the general procedure, pent-4-en-1-ol silyl ether (99.0 mg, 0.494 mmol) and catalyst **1** + **3** (3.5 mg, 0.0050 mmol, 1 mol%) were used. The reaction was conducted at 70 °C.

Table S-VIII-2b. Isomerization of pent-4-en-1-ol *tert*-butyldimethylsilylether at 70 °C.

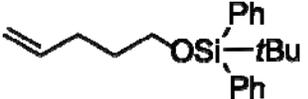
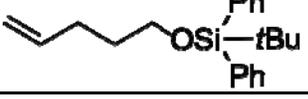
	Measured integrals in arbitrary units relative to internal standard = 10.0 units and (in bold) derived per cent yields of products and amount of starting 1-alkene						
Time	0 h	1 h	2 h	5 h	7 h	23 h	46 h
 (5.82 ppm)	40.52	14.83	6.62	2.26	1.29	1.63	1.49
 (4.99 ppm)	41.01	14.81	6.66	2.40	2.14	1.64	1.63
 (4.92 ppm)	40.88	14.95	6.56	2.39	2.12	1.83	1.91
units per proton ^a	40.80	14.83	6.61	2.35	1.85	1.70	1.67
% starting material remaining ^b	100	36.3	16.2	5.8	4.5	4.2	4.1
 (5.38-5.52 ppm)	0	52.68	66.90	75.23	74.77	75.62	73.77
units per proton ^a	0	26.34	33.45	37.62	37.39	37.81	36.89
% yield of product ^c	0	64.6	82.0	92.2	91.6	92.7	90.4

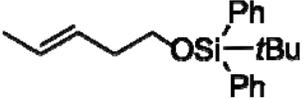
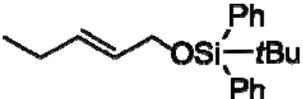
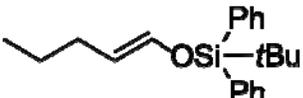
 (4.12 ppm)	0	0	0	0	trace	2.03	2.52
units per proton ^a	0	0	0	0	trace	1.02	1.26
% yield of isomer ^c	0	0	0	0	trace	2.5	3.1
	0	0	0	0	0	0	0
units per proton ^a	0	0	0	0	0	0	0
% yield of enol ether ^c	0	0	0	0	0	0	0

^aCalculated by taking the average of integrations of the specified resonances. ^bCalculated by dividing units per proton of starting material at time indicated by units per proton value at hour 0. ^cCalculated by dividing units per proton of product at time indicated by the units per proton value of starting material at hour 0.

S-VIII-3. Data for manuscript Table 2, entry 3: isomerization of pent-4-en-1-ol *tert*-butyldiphenylsilyl ether of using 2 mol% catalyst **1 and 6 mol% 4-(*tert*-butyl)-2-(diisopropylphosphino)-1-methyl-1*H*-imidazole at 40 °C in acetone-*d*₆.** Following general procedure, pent-4-en-1-ol *tert*-butyldiphenylsilyl ether (98.1 mg, 0.302 mmol) and 4-(*tert*-butyl)-2-(diisopropylphosphino)-1-methyl-1*H*-imidazole (4.9 mg, 0.019 mmol, 6.4 mol%) were combined with internal standard (0.6 mg) in acetone-*d*₆. After acquiring an initial spectrum catalyst **1** + **3** (4.4 mg, 0.0063 mmol, 2.1 mol%) was added. The reaction was conducted at 40 °C using an oil bath. At specified time points, ¹H NMR spectra were obtained.

Table S-VIII-3. Isomerization of pent-4-en-1-ol *tert*-butyldiphenylsilyl ether using 2 mol% catalyst **1** and 6 mol% imidazolylphosphine ligand at 40 °C.

	Measured integrals in arbitrary units relative to internal standard = 10.0 units and (in bold) derived per cent yields of products and amount of starting 1-alkene.				
Time	0 h	2 h	5 h	23 h	48 h
 (5.82 ppm)	54.35	32.65	18.18	4.59	2.81
	109.46	64.91	36.22	8.90	5.36

(4.99 - 4.92 ppm)					
units per proton ^a	54.60	32.52	18.13	4.50	2.72
% starting material remaining ^b	100	59.6	33.2	8.2	5.0
 (5.40-5.52 ppm)	0	43.17	69.40	95.99	98.57
units per proton ^a	0	21.59	34.70	48.00	49.29
% yield of product ^c	0	39.5	63.6	87.9	90.3
 (4.20 ppm)	0	0	0.25	0.72	1.06
units per proton ^a	0	0	0.12	0.36	0.53
% yield of isomer ^c	0	0	0.2	0.6	1.0
	0	0	0	0	0
units per proton ^a	0	0	0	0	0
% yield of silyl enol ether ^c	0	0	0	0	0

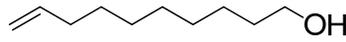
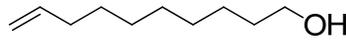
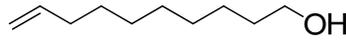
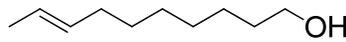
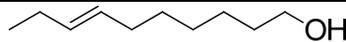
^a Calculated by taking the average of integrations of the specified resonances. ^b Calculated by dividing units per proton of starting material at time indicated by units per proton value at hour 0.

^c Calculated by dividing units per proton of product at time indicated by the units per proton value of starting material at hour 0.

VIII-4. Data for manuscript Table 2, entry 4: Isomerization of dec-9-en-1-ol at 70 °C.

Following the general procedure, dec-9-en-1-ol (83.2 mg, 0.532 mmol) and catalyst **1** + **3** (3.9 mg, 0.0055 mmol, 1 mol%) were used. The reaction was conducted at 70 °C.

Table S-VIII-4. Isomerization of dec-9-en-1-ol to (*E*)-dec-8-en-1-ol at 70 °C.

Time	Measured integrals in arbitrary units relative to internal standard = 10.0 units and (in bold) derived per cent yields of products and amount of starting 1-alkene					
	0 h	1 h	2 h	5 h	24 h	46 h
 (5.80 ppm)	55.71	19.09	8.42	2.32	1.75	1.53
 (4.98 ppm)	55.01	19.41	8.35	2.41	1.83	1.64
 (4.90 ppm)	56.65	19.30	8.31	2.37	1.82	1.68
units per proton ^a	55.81	19.27	8.36	2.37	1.80	1.62
% starting material remaining ^b	100	34.5	15.0	4.2	3.2	2.9
 (5.33-5.48 ppm)	0	73.16	95.52	106.12	106.34	106.36
units per proton ^a	0	36.58	47.76	53.06	53.17	53.18
% yield of product ^c	0	65.5	85.6	95.1	95.3	95.3
 (0.94 ppm)	0	0	0	3.58	11.93	15.75
units per proton ^a	0	0	0	1.20	3.98	5.25
% yield of product ^c	0	0	0	2.1	7.1	9.4

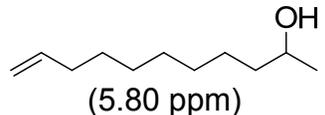
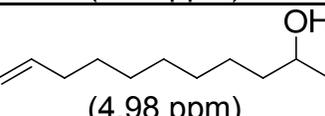
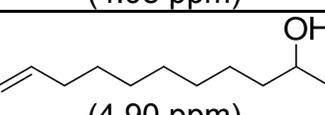
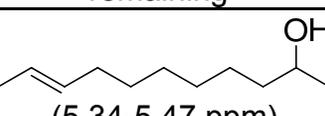
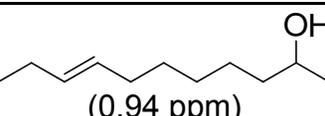
^aCalculated by taking the average of integrations of the specified resonances. ^bCalculated by dividing units per proton of starting material at time indicated by units per proton value at hour 0. ^cCalculated by dividing units per proton of product at time indicated by the units per proton value of starting material at hour 0.

VIII-5. Data for manuscript Table 2, entry 5: Isomerization of undec-10-en-2-ol at 40 °C. Following the general procedure, undec-10-en-2-ol (85.3 mg, 0.501 mmol) and catalyst **1** + **3** (3.6 mg, 0.0051 mmol, 1 mol%) were used. The reaction was conducted at 40 °C.

For undec-10-en-2-ol in the mixture: ¹H NMR (500 MHz, acetone-*d*₆) δ 5.80 (tdd, *J* = 7.0, 10.0, 17.0, 1H), 4.98 (dtd, *J* = 1.5, 2.0, 17.0, 1H), 4.90 (tdd, *J* = 1.5, 2.0, 10.0, 1H), 3.63-3.75 (m, 1H), 3.37 (d, *J* = 4.5, 1H), 2.04 (td, *J* = 7.0, 7.0, 2H), 1.33-1.48 (m, 4H), 1.31 (br s, 8H), 1.10 ppm (d, *J* = 6.0, 3H).

For the (*E*)-undec-9-en-2-ol in the mixture: ¹H NMR (500 MHz, acetone-*d*₆) δ 5.34-5.47 (m, 2H), 3.64-3.73 (m, 1H), 3.33 (d, *J* = 4.5, 1H), 1.92-2.00 (m, 2H), 1.61 (md, *J* = 5.0, 3H), 1.22-1.46 (m, 12H), 1.10 ppm (d, *J* = 6.0, 3H). ¹³C NMR (125.73 MHz, acetone-*d*₆) δ 132.41, 125.24, 67.64, 40.40, 33.34, 30.47, 30.43, 30.03, 26.67, 24.16, 18.12 ppm.

Table S-VIII-5. Isomerization of undec-10-en-2-ol to (*E*)-undec-9-en-2-ol at 40 °C.

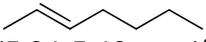
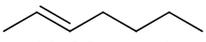
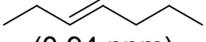
	Measured integrals in arbitrary units relative to internal standard = 10.0 units and (in bold) derived per cent yields of products and amount of starting 1-alkene					
Time	0 h	1 h	2 h	5 h	23 h	46 h
 (5.80 ppm)	25.80	21.67	16.45	11.25	1.50	0.61
 (4.98 ppm)	26.08	21.56	16.65	11.40	1.73	0.55
 (4.90 ppm)	26.02	21.85	16.68	11.40	1.70	0.56
units per proton ^a	25.97	21.69	16.59	11.35	1.64	0.57
% starting material remaining ^b	100	83.5	63.9	43.7	6.3	2.2
 (5.34-5.47 ppm)	0	8.64	14.03	27.66	48.52	50.73
units per proton ^a	0	4.32	7.02	13.83	24.26	25.37
% yield of product ^c	0	16.6	27.0	53.3	93.4	97.7
 (0.94 ppm)	0	0	0	0	0	trace
units per proton ^a	0	0	0	0	0	trace
% yield of product ^c	0	0	0	0	0	trace

^aCalculated by taking the average of integrations of the specified resonances. ^bCalculated by dividing units per proton of starting material at time indicated by units per proton value at hour 0. ^cCalculated by dividing units per proton of product at time indicated by the units per proton value of starting material at hour 0.

IX. Data for control experiments showing reaction of Cp*Ru catalyst 1 + 3 and internal alkenes

IX-1a. Data for isomerization of *E*-2-heptene using 1 mol% catalyst 1 at 40 °C in acetone-*d*₆. Following general procedure, *E*-2-heptene (49.3 mg, 0.502 mmol) and catalyst 1 + 3 (3.5 mg, 0.0050 mmol, 1 mol%) were used. Reaction was conducted at 40 °C using an oil bath. At specified time points, ¹H NMR spectra were obtained. For GC analysis, see next experiment done in protio acetone.

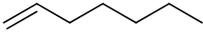
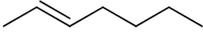
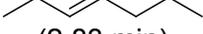
Table S-IX-1a. Yields determined by NMR in isomerization of *E*-2-heptene using 1 mol% catalyst 1 + 3 at 40 °C.

	Measured integrals in arbitrary units relative to internal standard = 10.0 units and (in bold) derived per cent yields of products and amount of starting 1-alkene.		
Time	0 h	22 h	165 h
 (5.80 ppm)	0	0.53	0.73
 (4.90-4.97 ppm)	0	1.10	1.52
units per proton ^a	0	0.54	0.75
% 1-alkene formed ^d	0	1.8	2.5
 (5.34-5.46 ppm) ^c	60.26	59.12	58.71
 (1.60 ppm)	90.34	88.24	86.17
units per proton ^a	30.12	29.47	28.98
% of <i>E</i> -2 remaining ^b	100	97.8	96.2
 (0.94 ppm)	0	0.88	3.1
units per proton ^a	0	0.29	1.03
% of <i>E</i> -3 ^d	0	1.0	3.4

^a Calculated by taking the average of integrations of the specified resonances. ^b Calculated by dividing units per proton of starting material at time indicated by units per proton value at hour 0. ^c Includes vinylic H for *E*-2, *E*-3 and *Z*-2, but *E*-2 dominates throughout. ^d Calculated by dividing units per proton of product at time indicated by the units per proton value of starting material at hour 0.

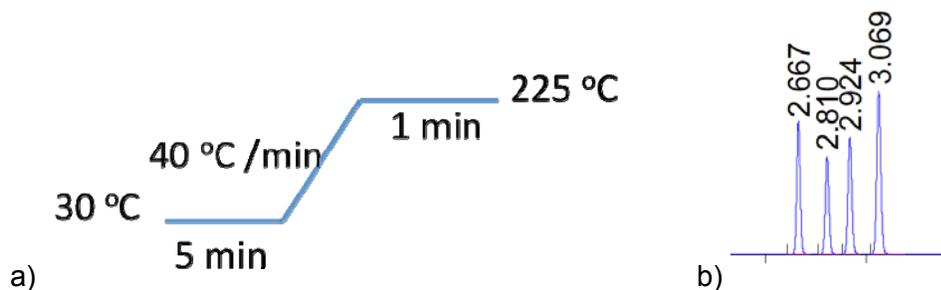
IX-2a. Data for isomerization of *E*-2-heptene using 1 mol% catalyst 1 + 3 at 40 °C in acetone-*h*₆. Following general procedure, *E*-2-heptene (49.8 mg, 0.507 mmol) and catalyst 1 + 3 (3.7 mg, 0.0053 mmol, 1 mol%) were used. Reaction was conducted at 40 °C oil bath. At specified time points, 5 μL of reaction mixture was removed under inert atmosphere for GC analysis. Because protio acetone was used, no NMR data are reported.

Table S-IX-2a. Ratios determined by GC in isomerization of *E*-2-heptene using 1 mol% catalyst at 40 °C.

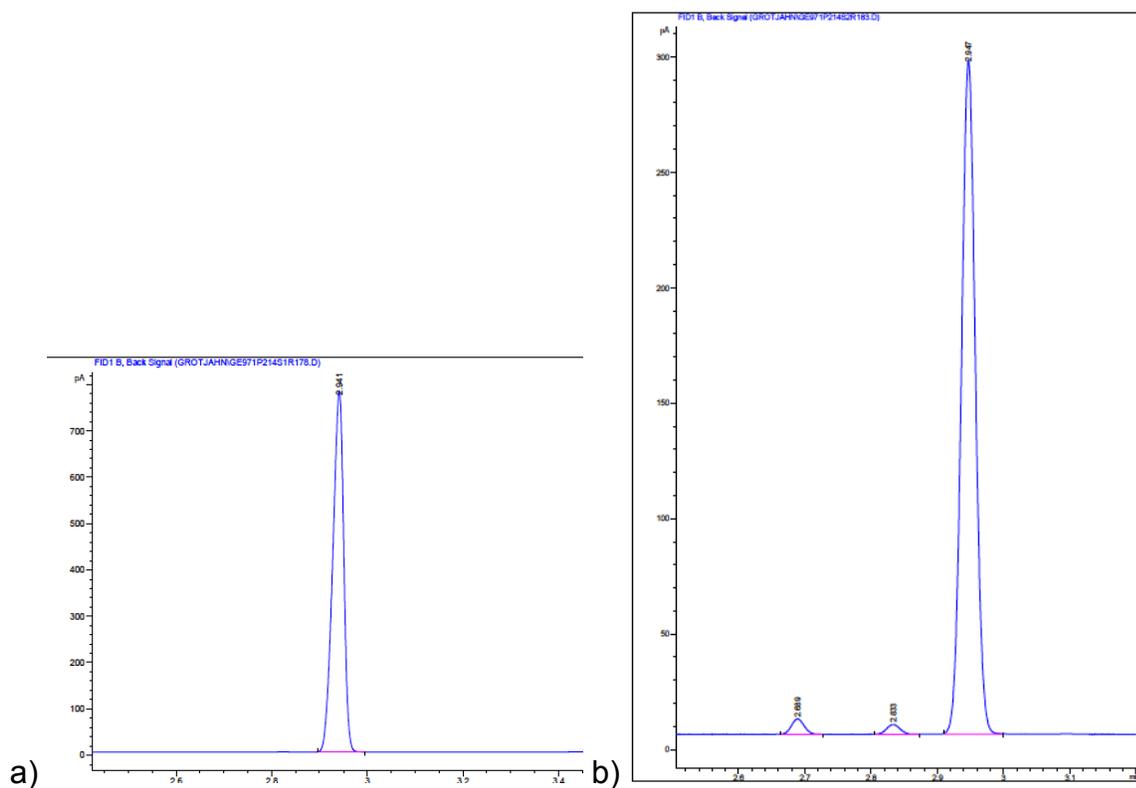
Time	0 h	48 h
 (2.68 min)	0	8.98
% 1-heptene ^a	0	2.0
 (2.94 min)	1246.55	426.70
% of <i>E</i> -2 ^a	100	96.6
 (2.83 min)	0	5.94
% of <i>E</i> -3 ^a	0	1.3
 (3.09 min)	0	0
% of <i>Z</i> -2 ^a	0	0
Total area	1246.55	441.62

^a Calculated by taking the ratios of integrations of the specified retention times.

Scheme S-IX-2a. A) Gas chromatography temperature program for C7 reaction mixtures. **B)** Gas chromatogram for authentic C7 mixture of 1-heptene, *E*-3-heptene, *E*-2-heptene, and *Z*-2-heptene respectively.

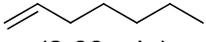
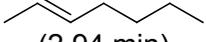
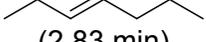


Scheme S-IX-2b. Gas chromatogram C7 reaction mixtures **a)** 0 h. **b)** 48 h.



IX-3a. Data for isomerization of *E*-3-heptene using 1 mol% catalyst 1 + 3 at 40 °C in acetone-*d*₆. Following general procedure, *E*-3-heptene (49.5 mg, 0.504 mmol) and catalyst 1 + 3 (3.6 mg, 0.0051 mmol, 1 mol%) were used. Reaction was conducted at 40 °C oil bath. At specified time points, ¹H NMR spectra were obtained and 5 μL of reaction mixture was removed under inert atmosphere for GC analysis.

Table S-IX-3a. Ratios determined by GC in isomerization of **E-3-heptene** using 1 mol% catalyst **1 + 3** at 40 °C.

Time	22 h	48 h	188 h
 (2.68 min)	0	0	0
% 1-heptene ^a	0	0	0
 (2.94 min)	8.51	10.99	23.73
% of E-2 ^a	0.9	1.3	1.8
 (2.83 min)	978.83	828.08	1278.85
% of E-3 ^a	99.1	98.7	98.2
 (3.09 min)	0	0	0
% of Z-2 ^a	0	0	0
Total area	987.34	839.07	1302.58

^a Calculated by taking the ratios of integrations of the specified retention times.

References

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