Supporting Information

Oxidation of Alkenes by Water with H₂ Liberation

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Table of Contents

General information ................................................................. S2

Products formation by reactions of alkenes with water ......................... S3

Procedures of the mechanistic experiments ........................................ S11

Oxidation of 1-octene by water .................................................. S15

NMR spectra of isolated products ................................................ S16

References .............................................................................. S28
General information

All of the reactions were performed in an atmosphere of purified nitrogen in a Braun glovebox or using standard Schlenk techniques, unless otherwise noted. All of the commercially available reagents were used as received. 1,4-Dioxane was purified prior to use by refluxing and distilling over Na/benzophenone under an argon atmosphere. Distilled water was purchased from Aldrich (HPLC grade) and was degassed prior to use by bubbling argon for at least 20 minutes. Complexes [Ru]-1, [Ru]-2 and [Ru]-3 were synthesized according to reported procedures. GC–MS analysis was carried out on HP 6890 (flame ionization detector and thermal conductivity detector) and HP 5973 (MS detector) instruments equipped with a 30 m column (Restek 5MS, 0.32 mm internal diameter) with a 5% phenylmethylsilicone coating (0.25 mm) and helium as carrier gas. Conversions and yields were determined in an average of two runs by GC analysis on Agilent Technologies 7890B (flame ionization detector) with nitrogen as the carrier gas while hydrogen gas was detected by GC analysis on HP 6890 (TCD detector) with nitrogen as the carrier gas. NMR spectra were recorded using Bruker Advance III 300 MHz, Advance III 400 MHz, or Advance 500 MHz spectrometers at 298 K. Chemical shifts were referenced to tetramethylsilane or the residual solvent peaks ($^1$H, $^{13}$C). Chemical shifts are reported in parts per million, and coupling constants ($J$) are reported in hertz.
Products formation by reactions of alkenes with water

**Acetophenone (2a):** A 25 mL Teflon-sealed tube equipped with a stir bar was charged with complex [Ru]-3 (2.6 mg, 0.0045 mmol), In(OTf)₃ (67.4 mg, 0.12 mmol), styrene (35 µL, 0.30 mmol), 2.0 mL of dioxane, and 1.0 mL of distilled water. The reaction mixture was stirred and heated at 150 °C (silicon oil bath temperature) at reflux in a sealed tube. After 36 hours, the reaction mixture was cooled down to room temperature.

**Hydrogen gas detection by GC:** The headspace was analyzed by GC with a TCD detector using N₂ as a carrier gas. As shown in Figure S1, only H₂ was detected by GC while no other gases were present in detectable amounts. H₂ was formed in 72% yield using argon as the internal standard. Then water (4.0 mL) was added to the reaction mixture and ethyl acetate (3 x 4.0 mL) was used to extract the organic compounds. The reaction mixture was analyzed by GC (FID detector) using mesitylene as an internal standard (83% yield). The effect of variation in [Ru]-3 loading is presented in Table S1.

**1H NMR (300 MHz, CDCl₃)** δ 7.89 (d, J = 7.5 Hz, 2H), 7.50 (t, J = 7.3 Hz, 1H), 7.39 (t, J = 7.6 Hz, 2H), 2.54 (s, 3H).

**13C{1H} NMR (75 MHz, CDCl₃)** δ 198.16, 137.12, 133.08, 128.55, 128.29, 26.58.

![Figure S1. GC analysis of the headspace gas](image-url)
Table S1. Effect of changing the loading of the ruthenium catalyst

| entry | [Ru]-3 | conv. (%) | yield (%) |
|-------|--------|-----------|-----------|
| 1     | 0.75 mol% | 90        | 74, 1     |
| 2     | 1.5 mol%  | 89        | 83, 4     |
| 3     | 3.0 mol%  | 91        | 67, 5     |

1-(4-(tert-Butyl)phenyl)ethan-1-one (2b):<sup>a</sup> A 25 mL Teflon-sealed tube equipped with a stir bar was charged with complex [Ru]-3 (2.6 mg, 0.0045 mmol), In(OTf)<sub>3</sub> (33.7 mg, 0.060 mmol), 4-tert-butylstyrene (95%, 58 µL, 0.30 mmol), 2.0 mL of dioxane, and 1.0 mL of distilled water. The reaction mixture was stirred and heated at 150 °C (silicon oil bath temperature) at reflux in a sealed tube. After 36 hours, the reaction mixture was cooled down to room temperature. Then water (4.0 mL) was added to the reaction mixture and ethyl acetate (3 x 4.0 mL) was used to extract the organic compounds. The reaction mixture was analyzed by GC (FID detector) using mesitylene as an internal standard (81% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.82 (d, J = 8.5 Hz, 2H), 7.40 (d, J = 8.5 Hz, 2H), 2.50 (s, 3H), 1.27 (s, 9H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 197.70, 156.80, 134.74, 128.27, 125.47, 35.08, 31.08, 26.44.

1-(p-Tolyl)ethan-1-one (2c):<sup>a</sup> A 25 mL Teflon-sealed tube equipped with a stir bar was charged with complex [Ru]-3 (2.6 mg, 0.0045 mmol), In(OTf)<sub>3</sub> (33.7 mg, 0.060 mmol), 4-methylstyrene (40 µL, 0.30 mmol), 2.0 mL of dioxane, and 1.0 mL of distilled water.
The reaction mixture was stirred and heated at 150 °C (silicon oil bath temperature at reflux in a sealed tube. After 36 hours, the reaction mixture was cooled down to room temperature. Then water (4.0 mL) was added to the reaction mixture and ethyl acetate (3 x 4.0 mL) was used to extract the organic compounds. The reaction mixture was analyzed by GC (FID detector) using mesitylene as an internal standard (93% yield) $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.79 (d, $J = 8.2$ Hz, 2H), 7.19 (d, $J = 7.9$ Hz, 2H), 2.51 (s, 3H), 2.34 (s, 3H). $^{13}$C {$^1$H} NMR (75 MHz, CDCl$_3$) $\delta$ 197.86, 143.86, 134.70, 129.22, 128.42, 26.51, 21.61.

1-(o-Toly)ethan-1-one (2d): $^6$ A 25 mL Teflon-sealed tube equipped with a stir bar was charged with complex [Ru]-3 (2.6 mg, 0.0045 mmol), In(OTf)$_3$ (67.4 mg, 0.12 mmol), 2-methylstylene (39 µL, 0.30 mmol), 2.0 mL of dioxane, and 1.0 mL of distilled water. The reaction mixture was stirred and heated at 150 °C (silicon oil bath temperature) at reflux in a sealed tube. After 36 hours, the reaction mixture was cooled down to room temperature. Then water (4.0 mL) was added to the reaction mixture and ethyl acetate (3 x 4.0 mL) was used to extract the organic compounds. The reaction mixture was analyzed by GC (FID detector) using mesitylene as an internal standard (40% yield). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.62 (d, $J = 7.8$ Hz, 1H), 7.31 (td, $J = 7.5$, 1.5 Hz, 1H), 7.18 (t, $J = 4.5$ Hz, 2H), 2.51 (s, 3H), 2.46 (s, 3H). $^{13}$C {$^1$H} NMR (75 MHz, CDCl$_3$) $\delta$ 201.73, 138.40, 137.64, 132.02, 131.49, 129.32, 125.67, 29.53, 21.56.

1-(4-Fluorophenyl)ethan-1-one (2e): $^4$ A 25 mL Teflon-sealed tube equipped with a stir bar was charged with complex [Ru]-3 (2.6 mg, 0.0045 mmol), In(OTf)$_3$ (67.4 mg, 0.12 mmol), 4-fluorostyrene (36 µL, 0.30 mmol), 2.0 mL of dioxane, and 1.0 mL of distilled water. The reaction mixture was stirred and heated at 150 °C (silicon oil bath temperature) at reflux in a sealed tube. After 36 hours, the reaction mixture was cooled down to room temperature. Then water (4.0 mL) was added to the reaction mixture and
ethyl acetate (3 × 4.0 mL) was used to extract the organic compounds. The reaction mixture was analyzed by GC (FID detector) using mesitylene as an internal standard (69% yield). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.99 – 7.82 (m, 2H), 7.15 – 7.00 (m, 2H), 2.52 (s, 3H). $^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$) δ 196.49, 165.77 (d, $J_{C-F} = 255.4$ Hz), 133.59 (d, $J_{C-F} = 3.0$ Hz), 130.93 (d, $J_{C-F} = 9.5$ Hz), 115.65 (d, $J_{C-F} = 22.0$ Hz), 26.53. $^{19}$F{$^1$H} NMR (282 MHz, CDCl$_3$) δ -106.34.

**1-(4-Chlorophenyl)ethan-1-one (2f):** A 25 mL Teflon-sealed tube equipped with a stir bar was charged with complex [Ru]-3 (2.6 mg, 0.0045 mmol), In(OTf)$_3$ (67.4 mg, 0.12 mmol), 4-chlorostyrene (36 µL, 0.30 mmol), 2.0 mL of dioxane, and 1.0 mL of distilled water. The reaction mixture was stirred and heated at 150 °C (silicon oil bath temperature) at reflux in a sealed tube. After 36 hours, the reaction mixture was cooled down to room temperature. Then water (4.0 mL) was added to the reaction mixture and ethyl acetate (3 × 4.0 mL) was used to extract the organic compounds. The reaction mixture was analyzed by GC (FID detector) using mesitylene as an internal standard (61% yield). $^1$H NMR (300 MHz, CDCl$_3$) δ 7.82 (d, $J = 8.6$ Hz, 2H), 7.37 (d, $J = 8.6$ Hz, 2H), 2.52 (s, 3H). $^{13}$C{$^1$H} NMR (75 MHz, CDCl$_3$) δ 196.81, 139.55, 135.42, 129.71, 128.87, 26.53.

**1-(4-(Diphenylphosphaneyl)phenyl)ethan-1-one (2g):** A 25 mL Teflon-sealed tube equipped with a stir bar was charged with complex [Ru]-3 (5.1 mg, 0.0090 mmol), In(OTf)$_3$ (101.1 mg, 0.18 mmol), diphenyl(4-vinylphenyl)phosphane (86.4 mg, 0.30 mmol), 2.0 mL of dioxane, and 1.0 mL of distilled water. The reaction mixture was stirred and heated at 150 °C (silicon oil bath temperature) at reflux in a sealed tube. After 36 hours, the reaction mixture was cooled down to room temperature. Then water (4.0 mL) was added to the reaction mixture and ethyl acetate (3 × 4.0 mL) was used to
extract the organic compounds. The reaction mixture was analyzed by GC (FID detector) using mesitylene as an internal standard (61% yield). $^1$H NMR (400 MHz, C$_6$D$_6$) δ 7.34 – 7.29 (m, 2H), 7.13 – 6.68 (m, 12H), 1.75 (s, 3H). $^{13}$C{$^1$H} NMR (101 MHz, C$_6$D$_6$) δ 196.13, 144.24 (d, $J_{C-P} = 15.2$ Hz), 137.39, 137.10 (d, $J_{C-P} = 11.8$ Hz), 134.36 (d, $J_{C-P} = 20.2$ Hz), 133.70 (d, $J_{C-P} = 18.9$ Hz), 129.30, 129.03, 128.96, 26.16. $^{31}$P{$^1$H} NMR (121 MHz, C$_6$D$_6$) δ -4.92.

**1-(3-Methoxyphenyl)ethan-1-one (2h):** A 25 mL Teflon-sealed tube equipped with a stir bar was charged with complex [Ru]-3 (2.6 mg, 0.0045 mmol), In(OTf)$_3$ (67.4 mg, 0.12 mmol), 3-methoxystyrene (42 µL, 0.30 mmol), 2.0 mL of dioxane, and 1.0 mL of distilled water. The reaction mixture was stirred and heated at 150 °C (silicon oil bath temperature) at reflux in a sealed tube. After 36 hours, the reaction mixture was cooled down to room temperature. Then water (4.0 mL) was added to the reaction mixture and ethyl acetate (3 x 4.0 mL) was used to extract the organic compounds. The reaction mixture was analyzed by GC (FID detector) using mesitylene as an internal standard (73% yield). The pure product (colorless oil, 28.7 mg, 64% yield) was obtained by flash column chromatography on silica gel (hexane : ethyl acetate = 100:1). $^1$H NMR (300 MHz, CDCl$_3$) δ 7.58-7.37 (m, 2H), 7.30 (t, $J = 7.9$ Hz, 1H), 7.04 (dd, $J = 8.0$, 2.2 Hz, 1H), 3.78 (s, 3H), 2.52 (s, 3H). $^{13}$C{$^1$H} NMR (75 MHz, CDCl$_3$) δ 197.95, 159.75, 138.42, 129.52, 121.09, 119.59, 112.26, 55.39, 26.70.

**1-(4-Methoxyphenyl)ethan-1-one (2i):** A 25 mL Teflon-sealed tube equipped with a stir bar was charged with complex [Ru]-3 (2.6 mg, 0.0045 mmol), In(OTf)$_3$ (1.7 mg, 0.0030 mmol), 4-methoxystyrene (40 µL, 0.30 mmol), 2.0 mL of dioxane, and 1.0 mL of distilled water. The reaction mixture was stirred and heated at 150 °C (silicon oil bath temperature) at reflux in a sealed tube. After 36 hours, the reaction mixture was cooled down to room temperature. Then water (4.0 mL) was added to the reaction mixture and
ethyl acetate (3 x 4.0 mL) was used to extract the organic compounds. The reaction mixture was analyzed by GC (FID detector) using mesitylene as an internal standard (74% yield). The pure product (pale yellow oil, 33.2 mg, 74% yield) was obtained by flash column chromatography on silica gel (hexane : ethyl acetate = 50:1). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.86 (d, $J$ = 8.9 Hz, 2H), 6.86 (d, $J$ = 8.9 Hz, 2H), 3.80 (s, 3H), 2.48 (s, 3H). $^{13}$C ($^1$H) NMR (75 MHz, CDCl$_3$) $\delta$ 196.77, 163.46, 130.56, 130.31, 113.65, 55.43, 26.30.

**Propiophenone (2j):**$^9$ A 25 mL Teflon-sealed tube equipped with a stir bar was charged with complex [Ru]-3 (2.6 mg, 0.0045 mmol), In(OTf)$_3$ (67.4 mg, 0.12 mmol), $\beta$-methyl styrene (38 $\mu$L, 0.30 mmol), 2.0 mL of dioxane, and 1.0 mL of distilled water. The reaction mixture was stirred and heated at 150 °C (silicon oil bath temperature) at reflux in a sealed tube. After 36 hours, the reaction mixture was cooled down to room temperature. Then water (4.0 mL) was added to the reaction mixture and ethyl acetate (3 x 4.0 mL) was used to extract the organic compounds. The reaction mixture was analyzed by GC (FID detector) using mesitylene as an internal standard (9% yield).

1-{[1,1'-Biphenyl]-4-yl}ethan-1-one (2k):$^{10}$ A 25 mL Teflon-sealed tube equipped with a stir bar was charged with complex [Ru]-3 (2.6 mg, 0.0045 mmol), In(OTf)$_3$ (67.4 mg, 0.12 mmol), 4-vinyl-1,1'-biphenyl (54.0 mg, 0.30 mmol), 2.0 mL of dioxane, and 1.0 mL of distilled water. The reaction mixture was stirred and heated at 150 °C (silicon oil bath temperature) at reflux in a sealed tube. After 36 hours, the reaction mixture was cooled down to room temperature. Then water (4.0 mL) was added to the reaction mixture and ethyl acetate (3 x 4.0 mL) was used to extract the organic compounds. The reaction mixture was analyzed by GC (FID detector) using mesitylene as an internal standard (86% yield). The pure product (white solid, 44.2 mg, 75% yield) was obtained by flash column chromatography on silica gel (hexane : ethyl acetate = 100:1). $^1$H NMR
(500 MHz, CDCl$_3$) $\delta$ 7.96 (d, $J = 8.4$ Hz, 2H), 7.62 (d, $J = 8.4$ Hz, 2H), 7.56 (d, $J = 7.1$ Hz, 2H), 7.40 (t, $J = 7.5$ Hz, 2H), 7.36 – 7.31 (m, 1H), 2.57 (s, 3H). $^{13}$C $^{1}$H NMR (126 MHz, CDCl$_3$) $\delta$ 197.76, 145.79, 139.87, 135.85, 128.94, 128.91, 128.22, 127.27, 127.22, 26.66.

1-(Naphthalen-2-yl)ethan-1-one (2l):$^{11}$ A 25 mL Teflon-sealed tube equipped with a stir bar was charged with complex [Ru]-3 (2.6 mg, 0.0045 mmol), In(OTf)$_3$ (67.4 mg, 0.12 mmol), 2-vinylnaphthalene (46.3 mg, 0.30 mmol), 2.0 mL of dioxane, and 1.0 mL of distilled water. The reaction mixture was stirred and heated at 150 °C (silicon oil bath temperature) at reflux in a sealed tube. After 36 hours, the reaction mixture was cooled down to room temperature. Then water (4.0 mL) was added to the reaction mixture and ethyl acetate (3 x 4.0 mL) was used to extract the organic compounds. The reaction mixture was analyzed by GC (FID detector) using mesitylene as an internal standard (78% yield). The pure product (white solid, 32.7 mg, 68% yield) was obtained by flash column chromatography on silica gel (hexane : ethyl acetate = 100:1). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.36 (s, 1H), 7.94 (dd, $J = 8.6$, 1.6 Hz, 1H), 7.87 (d, $J = 8.0$ Hz, 1H), 7.78 (dd, $J = 8.1$, 5.8 Hz, 2H), 7.54 – 7.40 (m, 2H), 2.62 (s, 3H). $^{13}$C $^{1}$H NMR (101 MHz, CDCl$_3$) $\delta$ 197.92, 135.60, 134.59, 132.56, 130.10, 129.52, 128.41, 128.38, 127.75, 126.73, 123.90, 26.57.

Norbornanone (3m):$^{12}$ A 25 mL Teflon-sealed tube equipped with a stir bar was charged with complex [Ru]-3 (2.6 mg, 0.0045 mmol), In(OTf)$_3$ (67.4 mg, 0.12 mmol), norbornene (28.2 mg, 0.30 mmol), 2.0 mL of dioxane, and 1.0 mL of distilled water. The reaction mixture was stirred and heated at 150 °C (silicon oil bath temperature) at reflux in a sealed tube. After 36 hours, the reaction mixture was cooled down to room temperature. Then water (4.0 mL) was added to the reaction mixture and ethyl acetate (3 x 4.0 mL) was used to extract the organic compounds. The reaction mixture was analyzed by GC (FID detector) using mesitylene as an internal standard (76% yield).
Cycloheptanone (3n): A 25 mL Teflon-sealed tube equipped with a stir bar was charged with complex [Ru]-3 (5.1 mg, 0.0090 mmol), In(OTf)₃ (101.1 mg, 0.18 mmol), cycloheptene (35 µL, 0.30 mmol), 2.0 mL of dioxane, and 1.0 mL of distilled water. The reaction mixture was stirred and heated at 150 °C (silicon oil bath temperature) at reflux in a sealed tube. After 72 hours, the reaction mixture was cooled down to room temperature. Then water (4.0 mL) was added to the reaction mixture and ethyl acetate (3 x 4.0 mL) was used to extract the organic compounds. The reaction mixture was analyzed by GC (FID detector) using mesitylene as an internal standard (29% yield).

Cycloheptanone (3o): A 25 mL Teflon-sealed tube equipped with a stir bar was charged with complex [Ru]-3 (5.1 mg, 0.0090 mmol), In(OTf)₃ (101.1 mg, 0.18 mmol), cyclooctene (35 µL, 0.30 mmol), 2.0 mL of dioxane, and 1.0 mL of distilled water. The reaction mixture was stirred and heated at 150 °C (silicon oil bath temperature) at reflux in a sealed tube. After 72 hours, the reaction mixture was cooled down to room temperature. Then water (4.0 mL) was added to the reaction mixture and ethyl acetate (3 x 4.0 mL) was used to extract the organic compounds. The reaction mixture was analyzed by GC (FID detector) using mesitylene as an internal standard (26% yield).
**Procedures of the mechanistic experiments**

**In(OT)$_3$ promoted reaction between styrene and water:** A 25 mL Teflon-sealed tube equipped with a stir bar was charged with In(OTf)$_3$ (67.4 mg, 0.12 mmol), styrene (35 µL, 0.30 mmol), 2.0 mL of dioxane, and 1.0 mL of distilled water. The reaction mixture was stirred and heated in a silicon oil bath at 150 °C (bath temperature) at reflux in a sealed tube. After 36 hours, the reaction mixture was cooled down to room temperature. Then water (4.0 mL) was added to the reaction mixture and ethyl acetate (3 x 4.0 mL) was used to extract the organic compounds. An internal standard (40 µL of mesitylene, 0.288 mmol) was added to the organic solution and the reaction mixture was analyzed by GC to determine the conversion and yields.

**Dehydrogenation of 1-phenylethanol:** A 25 mL Teflon-sealed tube equipped with a stir bar was charged with complex [Ru]-3 (2.6 mg, 0.0045 mmol), 1-phenylethanol (36 µL, 0.30 mmol), 2.0 mL of dioxane, and 1.0 mL of distilled water. The reaction mixture was stirred and heated at 150 °C (silicon oil bath temperature) at reflux in a sealed tube. After 36 hours, the reaction mixture was cooled down to room temperature. Then water (4.0 mL) was added to the reaction mixture and ethyl acetate (3 x 4.0 mL) was used to extract the organic compounds. An internal standard (40 µL of mesitylene, 0.288 mmol) was added to the organic solution and the reaction mixture was then analyzed by GC to determine the conversion and yield.

**Procedure for the $^{31}\text{P}^{(1}\text{H})$ NMR study:** In a J. Young NMR tube, dioxane (0.50 mL), complex [Ru]-3 (5.7 mg, 0.010 mmol) and 1-phenylethanol (12 µL, 0.10 mmol) were combined. The $^{31}\text{P}^{(1}\text{H})$ NMR spectra of the reaction mixture were recorded upon heating at 80 °C for 6 h, 120 °C for 6 h and 150 °C for 12 h (Figure S2).
Figure S2. $^{31}$P{$^1$H} NMR analysis of the reaction between complex [Ru]-3 and 1-phenylethanol.

**Isotopic labelling experiment:** A 25 mL Teflon-sealed tube equipped with a stir bar was charged with complex [Ru]-3 (2.6 mg, 0.0045 mmol), In(OTf)$_3$ (67.4 mg, 0.12 mmol), styrene (35 µL, 0.30 mmol), 0.50 mL of dioxane, and 0.25 mL of H$_2^{18}$O (97% $^{18}$O-labelled). The reaction mixture was stirred and heated at 150 °C (silicon oil bath temperature) at reflux in a sealed tube. After 36 hours, the reaction mixture was cooled down to room temperature. Then ethyl acetate (3 x 4.0 mL) was used to extract the organic compounds. An internal standard (40 µL of mesitylene, 0.288 mmol) was added to the organic solution and the reaction mixture was analyzed by GC and GC-MS to determine the conversion and yields. The MS spectrum of the ketone product is shown in Figure S3. The product was obtained in 67% yield and determined to be 94% $^{18}$O-labelled.
Figure S3. MS spectrum of the $^{18}$O-labeled ketone product.

**KIE determination experiment:** A 25 mL Teflon-sealed tube equipped with a stir bar was charged with complex $[\text{Ru}]$-3 (2.6 mg, 0.0045 mmol), In(OTf)$_3$ (67.4 mg, 0.12 mmol), styrene (35 µL, 0.30 mmol), 2.0 mL of dioxane, and 1.0 mL of distilled water. The reaction mixture was stirred and heated at 150 °C (silicon oil bath temperature) at reflux in a sealed tube. After 3 hours, the reaction mixture was cooled down to room temperature. Then water (4.0 mL) was added to the reaction mixture and ethyl acetate (3 x 4.0 mL) was used to extract the organic compounds. The reaction mixture was analyzed by GC (FID detector) using mesitylene as an internal standard. Using the same procedure, a similar experiment was conducted using D$_2$O instead of H$_2$O. The results are shown in Scheme S1 (approximately $k_{\text{H}}/k_{\text{D}} = 2.0$).

**Scheme S1. KIE Experiment**
[Ru]-3 catalyzed hydrogenation of styrene: A 100 mL Fisher Porter tube equipped with a stir bar was charged with complex [Ru]-3 (2.6 mg, 0.0045 mmol), In(OTf)_3 (67.4 mg or 0, 0.12 mmol or 0), styrene (35 µL, 0.30 mmol), 2.0 mL of dioxane, and 1.0 mL of H_2O. The tube was closed, taken out from the box and pressurized with 5 bar of hydrogen. The reaction mixture was stirred and heated at 150 °C (silicon oil bath temperature) at reflux in a sealed tube. After 36 hours, the reaction mixture was cooled down to room temperature. Then water (4.0 mL) was added to the reaction mixture and ethyl acetate (3 x 4.0 mL) was used to extract the organic compounds. An internal standard (40 µL of mesitylene, 0.288 mmol) was added to the organic solution and the reaction mixture was analyzed by GC (FID detector) to determine the conversion and yields. As shown in Scheme S2, ethylbenzene was obtained in 55% yield in the presence of In(OTf)_3 and 61% yield in the absence of In(OTf)_3.

Scheme S2

(a) \[
\begin{align*}
\text{Ph} & \xrightarrow{1.5 \text{ mol\% } [\text{Ru}]-3} \text{Ph} \\
\text{1a} & \xrightarrow{40 \text{ mol\% In(OTf)}_3} \text{3a}
\end{align*}
\]

Conv. 100%

5 atm of H_2

(b) \[
\begin{align*}
\text{Ph} & \xrightarrow{1.5 \text{ mol\% } [\text{Ru}]-3} \text{Ph} \\
\text{1a} & \xrightarrow{40 \text{ mol\% In(OTf)}_3} \text{3a}
\end{align*}
\]

Conv. 100%

5 atm of H_2

55%

61%
Oxidation of 1-octene by water

Reaction procedure: A 25 mL Teflon-sealed tube equipped with a stir bar was charged with complex [Ru]-3 (2.6 mg, 0.0045 mmol), In(OTf)₃ (67.4 mg, 0.12 mmol), 1-octene (47 µL, 0.30 mmol), 2.0 mL of dioxane, and 1.0 mL of distilled water. The reaction mixture was stirred and heated at 150 °C (silicon oil bath temperature) at reflux in a sealed tube. After 36 hours, the reaction mixture was cooled down to room temperature. Then water (4.0 mL) was added to the reaction mixture and ethyl acetate (3 x 4.0 mL) was used to extract the organic compounds. The reaction mixture was then analyzed by GC-MS. The GC spectrum of the reaction mixture and the MS spectrum of the major ketone product are shown in Figure S4.

Figure S4. GC-MS analysis of the reaction mixture
NMR Spectra of isolated products

1H NMR

13C{1H} NMR
**1H NMR**

2b

![1H NMR Spectrum]

**13C{1H} NMR**

![13C{1H} NMR Spectrum]
$^1$H NMR

$^{13}$C($^1$H) NMR
$^1$H NMR

$^{13}$C{${}^1$H} NMR
$^{19}\text{F}$$^{(1\text{H})}$ NMR

\[
\begin{array}{c}
\text{F} \\
\text{O} \\
\text{F}
\end{array}
\]

$^{1}\text{H}$ NMR

\[
\begin{array}{c}
\text{Cl} \\
\text{O} \\
\text{Cl}
\end{array}
\]

2f
$^{13}$C{$^1$H} NMR

$^1$H NMR
1H NMR

\[
\text{MeO} \quad \text{O}
\]

\[
\text{MeO} \quad \text{O}
\]

13C\{1H\} NMR
$^1\text{H NMR}$

$^{13}\text{C}[^1\text{H}]$ NMR
$^{1}H$ NMR

$^{13}C\{^{1}H\}$ NMR
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