Supporting Information

Regioselective Isomerization of 2,3-Disubstituted Epoxides to Ketones: An Alternative to the Wacker Oxidation of Internal Alkenes

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General Considerations

Methods and Instruments

Unless stated otherwise, all synthetic manipulations were carried out using standard Schlenk techniques under a nitrogen atmosphere or in an MBraun Unilab glovebox under an atmosphere of purified nitrogen. Reactions were carried out in oven-dried glassware cooled under vacuum. IR spectra were recorded on a Nicolet 380 FT-IR spectrometer. $^1$H NMR and $^{13}$C($^1$H) NMR spectra were recorded on a Varian 300, 400, or 500 MHz instrument at 22 °C with shifts reported relative to the residual solvent peak (CDCl$_3$: 7.26 ppm ($^1$H), and 77.16 ppm ($^{13}$C)). All $J$ values are given in Hertz. Deuterated chloroform was purchased from Cambridge Isotope Laboratories and stored over K$_2$CO$_3$.

Optical rotations were measured on a Perkin-Elmer 241 polarimeter, and are given in 10$^{-1}$ deg cm$^2$ g$^{-1}$. Gas chromatography (GC) analyses were performed on a Hewlett Packard 6890 gas chromatograph equipped with an Astec CHIRALDEX A-TA and a Supelco β-Dex$^\text{TM}$ 225 column or a Shimadzu GC-2010 Chromatograph equipped with a J&W Scientific Cyclodex-B column. Both were equipped with a flame ionization detector and used Helium (Airgas, UHP grade) as carrier gas. Quantitative GC analysis was performed by adding the internal standard dodecane to the reaction mixture. Response factors versus dodecane for the epoxides were obtained using the synthesized substrates, while the products’ response factors were obtained using commercially available materials. HRMS analyses were performed on a Thermo Scientific Exactive Orbitrap MS system with an Ion Sense DART ion source.

The initial rate kinetics experiments were conducted on a Freeslate Core Module 3 (CM3) robotic platform located inside an MBraun drybox. The experiment was designed and executed using Library Studio(TM) and Automation Studio(TM) software. All solutions were dispensed robotically using a syringe dispense.

Chemicals

Anhydrous 1,4-dioxane was purchased from Sigma-Aldrich and degassed via three freeze-pump-thaw cycles prior to use. Anhydrous toluene, dichloromethane (DCM), hexanes, diethyl ether, and tetrahydrofuran (THF) were purchased from Fischer Scientific and sparged vigorously with nitrogen for 40 minutes prior to first use. The solvents were further purified by passing them under nitrogen pressure through two packed columns of neutral alumina (tetrahydrofuran was also passed through a third column packed with activated 4Å molecular sieves) or through neutral alumina and copper(II) oxide (for toluene and hexanes). Tetrahydrofuran, diethyl ether, and dichloromethane were degassed via three freeze-pump-thaw cycles prior to use. All epoxides used in this study were dried over calcium hydride and degassed.
via three freeze-pump-thaw cycles prior to use. All non-dried solvents used were reagent grade or better and used as received.

All other chemicals were purchased from Aldrich, Alfa-Aesar, TCI America, Strem, or Macron and used as received. Flash column chromatography was performed with silica gel (particle size 40–64 µm, 230–400 mesh) using either mixtures of ethyl acetate and hexanes or mixtures of diethyl ether and pentane as eluent. Before GC analysis, the catalyst was removed using a plug of alumina (neutral, 80–200 mesh) using ether as eluent.

The following compounds were prepared according to literature procedures:

a) catalysts and catalyst precursors

NaCo(CO)$_4$

$rac$-3,3'"-((1E,1'E)-((1S,2S)-Cyclohexane-1,2-diylbis(azanylylidene))bis-(methanylylidene))bis(4'-(tert-butyl)-2',5,6'-trimethyl-[1,1'-biphenyl]-2-olate)aluminum chloride ($4$-Al-Cl)$^2$

$rac$-3,3"-((1E,1'E)-((1S,2S)-Cyclohexane-1,2-diylbis(azanylylidene))bis-(methanylylidene))bis(4'-(tert-butyl)-2',5,6'-trimethyl-[1,1'-biphenyl]-2-olate)aluminum chloride ($4$, ($S,S$)-Al-Cl) made analogously to $rac$-4$^2$

$[rac$-salcyAl(THF)$_2$][Co(CO)$_4$]$^{-}$ ($6$, salcy = $N,N'$-bis(3,5-di-tert-butyl-salicylidene)-1,2-cyclohexanediylamine)$^3$

3,3"-((1E,1'E)-((1S,2S)-Cyclohexane-1,2-diylbis(azanylylidene))bis-(methanylylidene))bis(2',4',5,6'-tetramethyl-[1,1'-biphenyl]-2-olate)aluminum chloride ($($S,S$)-7$-Al-Cl, made analogously to $rac$ catalyst reported)$^2$

3,3"-((1E,1'E)-((1S,2S)-Cyclohexane-1,2-diylbis(azanylylidene))bis-(methanylylidene))bis(2',4,5,6'-trimethyl-[1,1'-biphenyl]-2-olate)aluminum chloride ($($S,S$)-8$-Al-Cl, made analogously to $rac$ catalyst reported)$^2$

b) epoxides

$rac$-trans-2,3-diethyloxirane ($1e$)$^4$

$rac$-trans-2,3-dipropylxirane ($1d$)$^5$

$rac$-trans-2-ethyl-3-methyloxirane ($1e$)$^6$

$rac$-trans-2-methyl-3-propyloxirane ($1f$)$^5$

$rac$-trans-2-butyl-3-methyloxirane ($1g$)$^7$

$rac$-trans-2-methyl-3-pentyloxirane ($1a$)$^7$

$rac$-trans-2-hexyl-3-methyloxirane ($1h$)$^7$
*rac-trans*-2-butyl-3-ethylxirane (**1i**)⁸  
*rac-trans*-2-isopropyl-3-methyloxirane (**1j**)⁹  
*rac-trans*-butyldimethyl((trans-3-methyloxiran-2-yl)methoxy)silane (**1k**)¹⁰  
*rac-tert*-butyldimethyl(3-(trans-3-methyloxiran-2-yl)propoxy)silane (**1l**)²  
*rac-trans*-2-benzyl-3-methyloxirane (**1m**)²  
*rac-trans*-β-methylstyrene oxide (**1o**)¹¹  

c) epoxide precursors  
(E)-1-(but-2-en-1-yl)-4-methoxybenzene¹²  
(E)-1-(but-2-en-1-yl)-4-methylbenzene¹³  
(E)-1-(but-2-en-1-yl)-3-methylbenzene¹³  
(E)-1-(but-2-en-1-yl)-2-methylbenzene¹³
**Control Experiments**

![Diagram showing the reaction between Me<sup>13</sup>Pent and Catalyst (2 mol %) in Ether, 22 °C, 18 h, resulting in Me<sup>13</sup>Pent and Me<sup>13</sup>Pent + Me<sup>13</sup>Pent.](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>% Conv.</th>
<th>% Yield</th>
<th>2a : 3a&lt;sup&gt;a&lt;/sup&gt;</th>
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<td>&gt;99</td>
<td>99</td>
<td>13.5 : 1</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>&gt;99</td>
<td>85</td>
<td>1 : 1</td>
</tr>
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<td>3</td>
<td>4-Al-Cl</td>
<td>&lt; 1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>4-Al-Cl + NaBPh&lt;sub&gt;4&lt;/sub&gt;</td>
<td>&lt; 1</td>
<td>-</td>
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<td>NaCo(CO)&lt;sub&gt;4&lt;/sub&gt;</td>
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<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>Co&lt;sub&gt;2&lt;/sub&gt;(CO)&lt;sub&gt;8&lt;/sub&gt;</td>
<td>&lt; 1</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

<sup>a</sup>Determined by quantitative GC analysis versus dodecane as an internal standard.
Kinetic Data

Initial rate kinetics by GC analysis: Order in Catalyst

The kinetics experiments were conducted on a Freeslate Core Module 3 (CM3) robotic platform located inside an MBraun drybox. 20–200 μl (8 vials each) of a stock solution of 4 in THF (10 mM) was dispensed robotically into 2 mL GC vials containing disposable stir bars. Volatiles were then removed from the vials using a Speedvac vacuum centrifuge (40 °C, 45 minutes) attached to a liquid nitrogen trap. At the start of each kinetics experiment, the temperature in the reaction block was set to 20 °C and the stir rate was set to 300 rpm. A stock solution of epoxide 1a (0.25 M) and an internal standard (dodecane, 0.3 eq) in ether was made and 200 μl was dispensed robotically into 8 vials containing the catalyst and capped immediately. Each of the 8 identical vials was stopped sequentially at regular intervals by opening the vial and pipetting the contents into another 2 ml GC vial containing water-doped alumina and ether cooled to −32 °C. Each reaction mixture was run through a plug of alumina using ether to remove the catalyst and analyzed by gas chromatography. The concentrations of starting material and product were plotted over time (example see Figure S1). The rate of the disappearance of epoxide was compared to the rate of the appearance of ketone (2a + 3a) up to 10% conversion. This was repeated at the different starting concentrations of 4 (0.001, 0.003, 0.005, 0.007, 0.010 M) (Figure S2). The linear trend indicates that the reaction is first order in catalyst.

![Monitoring Concentration for Kinetics](image)

**Figure S1.** Plot of concentration of epoxide and ketone over time to calculate rate at [4] = 0.005 M.
Figure S2. Order in Catalyst 4 by initial rate kinetics.

Long term kinetics by GC analysis: Order in Epoxide

A solution of 4 in THF (100 μl, 10 mM) was dispensed robotically into 2 mL GC vials containing disposable stir bars. Volatiles were then removed from the vials using a Speedvac vacuum centrifuge (40 °C, 45 minutes) attached to a liquid nitrogen trap. A stock solution was made of 1a with an approximate epoxide concentration of 0.6 M in ether containing 0.3 equivalents of dodecane as an internal standard. Portions of this stock solution were diluted to make 0.4 M and 0.2 M stock solutions. At the start of each kinetics experiment, the temperature in the reaction block was set to 20 °C and the stir rate was set to 300 rpm. 200 μl of each standard was transferred to two separate catalyst vials using an Eppendorf 1000 μl (blue) reference hand pipettor (t = 0). All reactions in the set were quenched after being allowed to react for 3 hours by opening the vial and pipetting the contents into another 2 ml GC vial containing water-doped alumina and ether cooled to −32 °C. Each reaction mixture was run through a plug of alumina using ether to remove the catalyst and analyzed by gas chromatography. The molarity of total ketone product produced in that set time (as a proxy for reaction rate) was compared for the different starting concentrations of epoxide (Figure S3). This was repeated with epoxide 1c for 5 hours to reproduce the result. All three starting concentrations produced the same amount of ketone in the set time which indicates that the reaction is zeroth order in substrate.
Order in Epoxide

**Figure S3.** Order in Epoxide by long term kinetics.

**Kinetic Isotope Effect**

Procedure same as initial rate kinetics for order in catalyst, above. Only epoxide concentrations were compared because we didn’t have an independent source of deuterated ketone to make a GC calibration curve and response factor. Note that the slight variation in starting concentration is due to error measuring small amounts of epoxide.
Figure S4. Kinetic isotope effect raw data.

Product Inhibition Test

Using initial rate procedure above, product inhibition was tested by adding an equivalent of ketone (2-butanone) to the reaction and comparing the initial rate to the normal reaction conditions without the extra ketone added. Experimental data showed no decrease in rate (in fact a slight increase, though probably within error of the measurement) indicating that there is no product inhibition. Note that the slight variation in starting concentration is due to error measuring small amounts of epoxide.

\[
\text{2-Butanone} + \text{Me}^\text{nPent} \quad \overset{4 \text{ (2 mol \%)} \text{ Ether, 20 °C}}{\rightarrow} \quad \text{Me}^\text{nPent} + \text{Me}^\text{nPent}
\]
Figure S5. Product inhibition test raw data
**Isolation of Deuterated Ketones**

*2,2-d$_2$-3-Octanone + 3,3-d$_2$-2-Octanone (2a-d$_2$ + 3a-d$_2$) compared to 3-Octanone*

In a glove box, a 20 ml scintillation vial equipped with a Teflon-coated magnetic stir bar was charged with 4 (15.3 mg, 0.0151 mmol, 2.0 mol %) and ether (3 ml). After 1 minute of stirring at 22 °C, the vial was cooled to −32 °C for 10 minutes to minimize the amount of ether lost to evaporation while adding the epoxide. 2,3-d$_2$-trans-2-Methyl-3-pentyloxirane (1a-d$_2$, 96.4 mg, 0.740 mmol) was added by weight via a syringe. The vial was then sealed and left to stir overnight at room temperature. After 18 hours, the vial was taken out of the glove box and concentrated *in vacuo* at 0 °C. The residue was purified through a plug of alumina using pentane as eluent. The solution was concentrated again before preparing a sample for $^1$H NMR (CDCl$_3$, 400 MHz).

![NMR spectra](image)

**Figure S6.** $^1$H NMR spectra of isolated deuterated ketones versus 3-octanone.
## Kinetic Resolution Catalyst Optimization

\[ \text{Me}^{\text{Me}} \overset{\text{O}}{\text{Bn}} + \text{Me}^{\text{Me}} \overset{\text{O}}{\text{Bn}} \xrightarrow{5 \text{ mol} \% \text{Catalyst}} \text{THF} (0.5 \text{ M}), 22 \degree \text{C}, 2 \text{ h} \]

\[ \rightarrow \text{Me}^{\text{Me}} \overset{\text{O}}{\text{Bn}} + \text{Me}^{\text{Me}} \overset{\text{O}}{\text{Bn}} \]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>% Conv.</th>
<th>% ee</th>
<th>( k_{\text{rel}} ) (1(^{\text{st}}) order)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(S,S)-4</td>
<td>48</td>
<td>70</td>
<td>15</td>
</tr>
<tr>
<td>2</td>
<td>(S,S)-5</td>
<td>45</td>
<td>67</td>
<td>17</td>
</tr>
<tr>
<td>3</td>
<td>(S,S)-7(^b)</td>
<td>21</td>
<td>12</td>
<td>3</td>
</tr>
<tr>
<td>4</td>
<td>(S,S)-8(^b)</td>
<td>16</td>
<td>7</td>
<td>2</td>
</tr>
</tbody>
</table>

\(^a\) Determined by quantitative GC analysis versus dodecane as an internal standard. \(^b\) Catalyst formed in situ from corresponding Al-Cl and NaCo(CO)\(_4\) (1 : 1 ratio).
**Kinetic Resolution Data**

A standard solution of catalyst 5 (0.05 M, THF) and a standard solution of the epoxide (1.0 M, THF) with dodecane (0.3 eq) as an internal standard were made in a glovebox.

For epoxide 1m: 150 μl of the epoxide standard were put in each of three vials. 150 μl of the catalyst solution were added to each vial (t = 0). Aliquots were taken at various time intervals (0.25, 0.5, 0.75, 1, 2, 3, 4.5, 6, 8, 10, 20 hours), diluted in THF, and cooled in the glovebox freezer (-32 °C; the isomerization reaction is very slow at this temperature). The vials were subsequently taken out of the glovebox, the reaction mixture filtered through a plug of SiO$_2$ using ether to remove the catalyst and analyzed by chiral GC analysis. It was observed that when taking aliquots the reaction slowed down and did not achieve as high of conversions. The reason for this behavior is currently unclear. The two high conversion data points were done using the method for the other epoxides (see below).

For other epoxides: 50 μl of the catalyst solution was added to multiple vials and cooled (−32 °C) for 10 minutes. 50 μl of the epoxide standard was added to the catalyst vials, which were then allowed to stir at room temperature inside the glovebox. Vials were stopped sequentially (such that each data point comes from a different reaction vial) by opening to air and run through a plug of alumina using ether to remove the catalyst. Conversion and % ee data was collected using chiral GC analysis.

Representative GC traces are included to show how % ee of the remaining epoxides changes over time.

The identity of the remaining epoxide enantiomer for *trans*-2-benzyl-3-methylxirane (1m) was determined by comparison to an independently synthesized sample of (S,S)-2-benzyl-3-methylxirane.$^2$ All substituted benzyl epoxides were assumed to react similarly and elute in the same order.
Kinetic Resolution of 1m (Me/Bn)

Simulated $k_{rel} = 17$

Experimental Data

Epoxide % ee

% Conversion

83% ee

67% ee
Figure S7. A) Kinetic resolution plot and B) GC traces for epoxide 1m.
Figure S8. A) Kinetic resolution plot and B) GC traces for epoxide 1p.
A

Kinetic Resolution of 1q (Me/m-MeBn)

Simulated $k_{rel} = 21$

Experimental Data

Epoxide % ee

% Conversion

B

63% ee

89% ee
Figure S9. A) Kinetic resolution plot and B) GC traces for epoxide 1q.

A

**Kinetic Resolution of 1r (Me/p-MeBn)**

- Simulated $k_{rel} = 18$
- Experimental Data
Figure S10. A) Kinetic resolution plot and B) GC traces for epoxide 1r.
A

Kinetic Resolution of $1n$ (Me/$p$-OMeBn)

Simulated $k_{rel} = 19$

Experimental Data

Epoxide % ee vs. % Conversion

B

61% ee

92% ee
Figure S11. A) Kinetic resolution plot and B) GC traces for epoxide 1n.

98% ee

>99% ee
**Synthetic Procedures**

**General procedure A: Epoxidation of alkenes to epoxides using \( m \)CPBA**

Under ambient atmosphere, \( m \)CPBA (Aldrich, \( \leq 77 \% \)) was added in portions at 0 °C to a solution of the corresponding alkene in DCM and the resulting mixture was stirred at room temperature until TLC analysis indicated complete consumption of the alkene. After destroying excess \( m \)CPBA by adding aqueous NaHSO\(_3\), the reaction mixture was filtered through celite, the organic phase washed with NaHCO\(_3\) (sat., aq., 3x), dried with sodium sulfate, filtered, and concentrated under reduced pressure.

**General procedure B: Kumada coupling of 2-bromophenols with 4-(tert-butyl)-2,6-dimethylphenyl magnesium bromide**

The appropriate brominated phenol was added dropwise to a mixture of sodium hydride (Aldrich, dry, 95%) and THF at 0 °C, followed by stirring at 22 °C for 10 minutes. Pd(OAc)\(_2\) (Strem, \( \geq 98 \% \)) was added, followed by 4-(tert-butyl)-2,6-dimethylphenyl magnesium bromide\(^{14} \) (1 M, THF), and the resulting mixture was refluxed for 12 h. Upon cooling to 0 °C, H\(_2\)O was carefully added to destroy any residual Grignard reagent and sodium hydride. HCl (2 M, aq.) followed by celite were added, and the resulting mixture was filtered through a pad of celite. The resulting phases were separated and the aqueous phase extracted with Et\(_2\)O (3x). The combined organic layers were washed with brine, dried with sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified via flash column chromatography (ethyl acetate/hexanes).

**General procedure C: Formylation of 2-arylphenols to the corresponding salicylaldehyde derivatives**

Methylmagnesium bromide (Acros, 3 M, Et\(_2\)O) was added slowly to the corresponding coupled phenol in THF at 0 °C. After warming to 22 °C, toluene, triethylamine, and paraformaldehyde were added, and the resulting reaction mixture stirred at 80 °C for 12 h. After cooling to 0 °C, H\(_2\)O and then HCl (2 M, aq.) were added, and the resulting phases were separated. The aqueous phase was extracted with Et\(_2\)O (3x). The combined organic layers were washed with brine, dried with sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified via flash column chromatography (ethyl acetate/hexanes) or recrystallization.

**General procedure D: Imine condensation of salicylaldehydes onto (1S,2S)-1,2-diaminocyclohexane**

The corresponding salicylaldehyde, (1S,2S)-1,2-diaminocyclohexane, and ethanol were mixed and then refluxed for 18 h. After allowing the reaction mixture to reach 22 °C, the resulting precipitate was
isolated by filtration, washed with a small amount of cold methanol and pentane, and then dried in vacuo at 80 °C.

**General procedure E: Isomerization of epoxides with quantitative GC yield**

In a glove box, a 1 fluid dram glass vial equipped with a Teflon-coated magnetic stir bar was charged with 4, dodecane, and ether. After 1 minute of stirring at 22 °C, the vial was cooled to −32 °C for 10 minutes to minimize the amount of ether lost to evaporation while adding the epoxide. The corresponding epoxide was added by weight via a syringe. The vial was then sealed and left to stir overnight at room temperature. After 18 hours, a drop of the reaction mixture was diluted with ether and passed through a neutral alumina plug to remove the catalyst before being subjected to quantitative GC analysis.

**General procedure F: Isomerization of epoxides with isolation**

In a glove box, a 20 ml scintillation vial equipped with a Teflon-coated magnetic stir bar was charged with 4 and ether. After 1 minute of stirring at 22 °C, the vial was cooled to −32 °C for 10 minutes to minimize the amount of ether lost to evaporation while adding the epoxide. The corresponding epoxide was added by weight via a syringe. The vial was then sealed and left to stir overnight at room temperature. After 18 hours, the vial was taken out of the glove box and concentrated in vacuo at 0 °C. The residue was purified by flash column chromatography (silica gel, pentane/ether).
Synthesis of Starting Materials

**rac-trans-2-Methyl-3-[(4-methoxyphenyl)methyl]-oxirane (1n)**

Following general procedure A, (E)-1-(but-2-en-1-yl)-4-methoxybenzene (1.40 g, 8.63 mmol) was treated with mCPBA (2.55 g, 11.4 mmol) in DCM (10 ml) to give **1n** (1.15 g, 75%) as a colorless oil. **^1H NMR** (400 MHz, CDCl₃): δ 7.15 (m, 2H), 6.85 (m, 2H), 3.80 (s, 3H), 2.65–2.95 (m, 4H), 1.30 (d, J = 5.1, 3H). **^13C[^1H] NMR** (101 MHz, CDCl₃): δ 158.5, 130.0, 129.6, 114.1, 60.0, 55.4, 54.6, 37.6, 17.7. **IR** (neat, cm⁻¹): 2964, 2932, 2834, 1612, 1511, 1243, 1177, 1034, 823, 729. **HRMS (DART) m/z** calculated for C₁₁H₁₅O⁺ (M + H)⁺ 179.10666, found 179.105894.

**rac-trans-2-Methyl-3-[(2-methylphenyl)methyl]-oxirane (1p)**

Following general procedure A, (E)-1-(but-2-en-1-yl)-2-methylbenzene (1.79 g, 12.2 mmol) was treated with mCPBA (3.63 g, 16.2 mmol) in DCM (14 ml) to give **1p** (1.68 g, 85%) as a colorless oil. **^1H NMR** (400 MHz, CDCl₃): δ 7.11–7.23 (m, 4H), 2.97 (dd, J = 14.5, 5.0, 1H), 2.88 (td, J = 5.2, 2.0, 1H), 2.73–2.85 (m, 2H), 2.32 (s, 3H), 1.31 (d, J = 5.3, 3H). **^13C[^1H] NMR** (101 MHz, CDCl₃): δ 136.5, 135.9, 130.3, 129.5, 126.8, 126.2, 59.1, 54.8, 35.6, 19.8, 17.7. **IR** (neat, cm⁻¹): 2967, 2924, 1494, 1446, 1378, 741, 726. **HRMS (DART) m/z** calculated for C₁₁H₁₅O⁺ (M + H)⁺ 163.11174, found 163.110998.

**rac-trans-2-Methyl-3-[(3-methylphenyl)methyl]-oxirane (1q)**

Following general procedure A, (E)-1-(but-2-en-1-yl)-3-methylbenzene (1.63 g, 11.1 mmol) was treated with mCPBA (3.31 g, 14.8 mmol) in DCM (13 ml) to give **1q** (1.51 g, 84%) as a colorless oil. **^1H NMR** (400 MHz, CDCl₃): δ 7.19 (t, J = 7.8, 1H), 6.98–7.06 (m, 3H), 2.80–2.90 (m, 3H), 2.74 (dd, J = 15.8, 6.9, 1H), 2.32 (s, 3H), 1.29 (d, J = 5.1, 3H). **^13C[^1H] NMR** (101 MHz, CDCl₃): δ 138.2, 137.5, 129.8, 128.5, 127.4, 126.0, 59.9, 54.8, 38.5, 21.5, 17.7. **IR** (neat, cm⁻¹): 2979, 2921, 1608, 1488, 1445, 1378, 950, 860, 759, 698. **HRMS (DART) m/z** calculated for C₁₁H₁₅O⁺ (M + H)⁺ 163.11174, found 163.11094.

**rac-trans-2-Methyl-3-[(4-methylphenyl)methyl]-oxirane (1r)**
Following general procedure A, (E)-1-(but-2-en-1-yl)-4-methylbenzene (1.38 g, 9.45 mmol) was treated with mCPBA (2.83 g, 12.6 mmol) in DCM (20 ml) to give 1r (1.34 g, 87%) as a colorless oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.12 (pseudo s, 4H), 2.63–2.95 (m, 4H), 2.33 (s, 3H), 1.30 (d, \(J = 5.1\), 3H). \(^{13}\)C\{\(^1\)H\} NMR (101 MHz, CDCl\(_3\)): \(\delta\) 136.2, 134.4, 129.3, 128.9, 59.9, 54.7, 38.1, 21.2, 17.7. IR (neat, cm\(^{-1}\)): 2979, 2922, 1515, 1446, 1378, 952, 867, 803, 723. HRMS (DART) \(m/z\) calculated for C\(_{11}\)H\(_{15}\)O\(^+(\text{M + H})^+\) 163.11174, found 163.11093.

2,3-\(d_2\)-cis-2-Octene (SM1)\(^15\)

\[\text{\begin{array}{c} \text{D} \\ \text{D} \end{array}} \]

2-Octyne (2.80 g, 25.5 mmol) was added to a flask charged with Lindlar’s catalyst (1.0 g) and pentane (43 ml). D\(_2\) gas (Cambridge Isotope, D = 99.6%) was bubbled through the reaction mixture at room temperature for 4 hours. The black solid was filtered off using celite and the resulting clear solution was concentrated in vacuo at 0 °C to give the title compound (1.78 g, 62%) as a colorless oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 5.41 (residual \(^1\)H signal in deuterated positions), 2.03 (m, 2H), 1.60 (m, 3H), 1.31 (m, 6H), 0.90 (t, \(J = 6.4\), 3H). \(^{13}\)C\{\(^1\)H\} NMR (101 MHz, CDCl\(_3\)): \(\delta\) 130.6 (pseudo t, \(J_{\text{C-D}} = 23.1\)), 123.3 (pseudo t, \(J_{\text{C-D}} = 23.4\)), 31.7, 29.4, 26.9, 22.8, 14.2, 12.7. IR (neat, cm\(^{-1}\)): 2938, 2923, 2856, 2247, 1633, 1456, 1377, 1189, 727. HRMS (DART) \(m/z\) calculated for C\(_8\)H\(_{13}\)D\(_2\)\(^+(\text{M – H})^+\) 113.12938, found 113.12963.

\((\text{rel-R,R})\)-2,3-\(d_2\)-3-Chloro-2-octanol and 2,3-\(d_2\)-2-chloro-3-octanol (SM2)\(^16\)

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

Deuterated alkene SM1 (2.95 g, 25.8 mmol) was taken up in acetone:water (5.5 : 1, 84 ml) and cooled to 0 °C. Trichloroisocyanuric acid (2.33 g, 10.0 mmol) was added in portions. The reaction mixture was warmed to room temperature and stirred for 2.5 hours before quenching with saturated NaHSO\(_3\). The solution was filtered through celite to remove the white precipitate, extracted with DCM, washed with brine, dried over Na\(_2\)SO\(_4\), and concentrated in vacuo to yield the product mixture (2.54 g, 59%) as a colorless oil. \(^{13}\)C\{\(^1\)H\} NMR (101 MHz, CDCl\(_3\)): \(\delta\) 74.7 (pseudo triplet, \(J_{\text{C-D}} = 21.7\)), 69.9 (overlapping pseudo triplet, \(J_{\text{C-D}} = 22.0\)), 69.7 (overlapping pseudo triplet, \(J_{\text{C-D}} = 22.8\)), 63.0 (pseudo triplet, \(J_{\text{C-D}} = 22.8\)), 34.3, 34.0, 31.8, 31.3, 26.2, 25.3, 22.5, 21.4, 20.0, 14.03, 14.00. IR (neat, cm\(^{-1}\)): 3395 (br),
2958, 2929, 2860, 1699, 1595, 1455, 1377, 1154, 932, 766, 727, 665. HRMS (DART) m/z calculated for C₈H₁₅D₂O⁺ (M – Cl)⁺ 131.13995, found 131.13999. H NMR (400 MHz, CDCl₃):

**A Schlenk flask was charged with triphenylphosphine (4.2 g, 21 mmol). Dry THF (60 ml) was cannula transferred to the flask, which was then cooled to 0 °C. Diisopropylazodicarboxylate (5.2 ml, 20 mmol) was added dropwise to the solution, which turned from clear to milky yellow. The mixture of chlorohydrins (SM2, 2.27 g, 13.6 mmol) was added followed by glacial acetic acid (1.3 ml, 23 mmol). The clear gold reaction was stirred at room temperature under a flow of nitrogen overnight then concentrated in vacuo. Hexanes were added and the resulting white solid was filtered off. After re-concentrating, the product was purified by flash column chromatography (hexanes:ether 10 : 1) to yield a 3 : 2 mixture of two regioisomers (1.46 g, 51%) as a colorless oil. C{¹H} NMR (101 MHz, CDCl₃): δ 170.4, 170.2, 75.9 (pseudo triplet, J₄D = 22.6), 71.9 (pseudo triplet, J₅D = 22.6), 64.3 (pseudo triplet, J₆D = 23.1), 57.8 (pseudo triplet, J₇D = 23.3), 34.0, 31.6, 31.2, 30.0, 26.2, 24.9, 22.48, 22.47, 21.1, 20.9, 20.2, 15.1, 13.96, 13.95. IR (neat, cm⁻¹): 2927, 2860, 1737 (sharp), 1455, 1368, 1238, 1021, 936. HRMS**
(DART) \( m/z \) calculated for \( \text{C}_{10}\text{H}_{18}\text{D}_{2}\text{O}\text{Cl}^+ \) (M + H)\(^+\) 209.12719, found 209.12772. \(^1\)H NMR (400 MHz, CDCl\(_3\)):

\[ \text{\begin{figure} \centering \includegraphics[width=\textwidth]{figure.png} \caption{\textbf{2,3-d}_2\text{-trans-2-Methyl-3-pentyloxirane (1a-d\(_2\))}} \end{figure}} \]

Potassium carbonate (6.04 g, 43.7 mmol) was suspended in methanol (15.5 ml). The mixture of chloroacetates (SM3, 1.21 g, 5.81 mmol) was added to the reaction dropwise and stirred at room temperature for 1.5 hours. The methanol was removed \textit{in vacuo} before adding water and DCM, extracting with DCM (2x), drying over NaSO\(_4\), and concentrating at 0 °C to give the product (0.673 g, 89%) as a colorless oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 2.72 (q, \( J = 5.3 \), deuterated position), 2.61 (t, \( J = 5.4 \), deuterated position), 1.34–1.57 (m, 4H), 1.18–1.34 (m, 7H), 0.88 (m, 3H). \(^{13}\)C\(^{\text{\(1\)}}\)H NMR (101 MHz, CDCl\(_3\)): \( \delta \) 59.2 (pseudo triplet, \( J_{C,D} = 25.9 \)), 54.0 (pseudo triplet, \( J_{C,D} = 26.1 \)), 31.8, 31.6, 25.6, 22.5, 17.4, 13.9. IR (neat, cm\(^{-1}\)): 2956, 2928, 2858, 1455, 1375, 1132, 918, 770, 732. HRMS (DART) \( m/z \) calculated for \( \text{C}_8\text{H}_{15}\text{D}_2\text{O}^+ \) (M + H)\(^+\) 131.13995, found 131.14060.

\[ \text{4',5-di(Tert-butyl)-2',6'-dimethyl-[1,1'-biphenyl]-2-ol (SM4)}} \]
Following general procedure B, 2-bromo-4-(tert-butyl)phenol (3.30 g, 14.4 mmol) was treated with sodium hydride (0.480 g, 20.0 mmol) in THF (24 ml), followed by addition of Pd(OAc)$_2$ (0.161 g, 0.717 mmol, 5 mol %), and 4-(tert-butyl)-2,6-dimethylphenyl magnesium bromide (0.92 M THF, 25 ml, 23 mmol) to give SM$_4$ (2.79 g, 62%) as a white powder. MP 86–87 °C. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.29 (dd, $J = 8.5, 2.5$, 1H), 7.20 (s, 2H), 7.06 (d, $J = 2.5$, 1H), 6.93 (d, $J = 8.5$, 1H), 4.51 (s, 1H), 2.08 (s, 6H), 1.37 (s, 9H), 1.31 (s, 9H). $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 151.2, 150.2, 143.5, 137.6, 132.5, 127.2, 125.9, 125.6, 125.1, 114.4, 34.6, 34.3, 31.8, 31.5, 20.8. IR (neat, cm$^{-1}$): 3522, 3026, 2956, 2864, 1498, 1360, 1220, 1164, 1021, 871, 820, 716. HRMS (DART) $m/z$ calculated for C$_{22}$H$_{30}$O$^+$ (M$^+$) 310.22912, found 310.22899.

2-Hydroxy-4′,5-di(tert-butyl)-2′,6′-dimethyl-[1,1′-biphenyl]-3-carbaldehyde (SM$_5$)

Following general procedure C, 4′,5-di(tert-butyl)-2′,6′-dimethyl-[1,1′-biphenyl]-2-ol (SM$_4$, 2.74 g, 8.83 mmol) was treated with methylmagnesium bromide (3 M ether, 3.6 ml, 10.8 mmol) in THF (24 ml), followed by addition of toluene (45 ml), triethylamine (2.2 ml, 16 mmol), and paraformaldehyde (0.766 g, 25.5 mmol). The product was purified via flash column chromatography (hexanes/Et$_2$O) to give SM$_5$ (2.48 g, 83%) as a white powder. MP 123–124 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 11.04 (s, 1H), 9.96 (s, 1H), 7.53 (d, $J = 2.5$, 1H), 7.44 (d, $J = 2.5$, 1H), 7.15 (2H), 2.06 (s, 6H), 1.35 (s, 9H), 1.34 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 197.1, 156.9, 150.5, 142.8, 136.8, 136.2, 133.4, 129.5, 128.9, 124.6, 120.2, 124.2, 125.9, 34.5, 34.4, 31.6, 31.4, 20.9. IR (neat, cm$^{-1}$): 2958, 2866, 1649, 1451, 1272, 1219, 1091, 864, 705. HRMS (DART) $m/z$ calculated for C$_{23}$H$_{31}$O$_2^+$ (M$^+$ + H$^+$) 339.23186, found 339.23064.

3,3″-((1E,1′E)-((1S,2S)-Cyclohexane-1,2-diylbis(azanylylidene))bis(methyanylylidene))-bis(4′,5-di(tert-butyl)-2′,6′-dimethyl-[1,1′-biphenyl]-2-ol) (SM$_6$)
Following general procedure D, 2-hydroxy-4',5-di(tert-butyl)-2',6'-dimethyl-[1,1'-biphenyl]-3-carbaldehyde (SM5, 0.676 g, 2.00 mmol) was treated with (S,S)-cyclohexyldiammine (0.117 g, 1.02 mmol) in ethanol (8 ml). The filtered solid was recrystallized from toluene to give SM6 (0.642 g, 85 %) as a yellow powder. 

**MP >200 °C.**

**1H NMR** (500 MHz, CDCl3): δ 13.51 (s, 2H), 8.28 (s, 2H), 7.17 (d, J = 2.1, 4H), 7.15 (m, 2H), 7.11 (d, J = 2.4, 2H), 3.23 (m, 2H), 2.10 (s, 6H), 1.97 (s, 6H), 1.93 (m, 2H), 1.85 (m, 2H), 1.66 (m, 2H), 1.44 (m, 2H), 1.37 (s, 18H), 1.26 (s, 18H).

**13C{1H} NMR** (126 MHz, CDCl3): δ 165.3, 155.9, 149.7, 141.0, 136.1, 136.0, 134.7, 131.3, 128.2, 126.5, 124.4, 124.3, 117.8, 72.7, 34.3, 34.0, 33.0, 31.5, 31.4, 24.2, 20.9, 20.8. 

**IR** (neat, cm⁻¹): 2951, 2865, 1626, 1449, 1361, 1272, 1225, 1154, 1093, 866, 823, 774, 727, 709. 

**HRMS** (DART) m/z calculated for C_{52}H_{70}N_{12}O_{12} (M + H)^+ 755.55101, found 755.54811.

**Specific rotation**: [α]_D^20 = +376 (c = 0.0055, CHCl₃).

3,3′′-((1E,1′E)-((1S,2S)-Cyclohexane-1,2-diylbis(azanylylidene))bis(methyanylylidene))-bis(4',5-di(tert-butyl)-2',6'-dimethyl-[1,1'-biphenyl]-2-olate)aluminum cobaltate ((S,S)-5)

Et₂AlCl (Aldrich, 0.98 M, hexanes, pyrophoric, 0.994 M, 900 μl, 0.260 mmol) was added to a solution of 3,3′′-((1E,1′E)-((1S,2S)-cyclohexane-1,2-diylbis(azanylylidene))bis(methyanylylidene))-bis(4',5-di(tert-butyl)-2',6'-dimethyl-[1,1'-biphenyl]-2-ol) (SM6, 0.611 g, 0.810 mmol) in DCM (6 ml) at 0 °C. The resulting solution was stirred at 22 °C for 12 h. Volatiles were removed and dried in vacuo overnight to give the corresponding Al-Cl (0.614 g, 93%) as a yellow solid, which was used directly.

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S30
without further purification or isolation. Al-Cl (0.0995 g, 0.122 mmol) was mixed with NaCo(CO)$_4$ (0.0255 g, 0.131 mmol) in THF (3 ml) for 3.5 hours in a glovebox at ambient temperature. The cloudy orange solution was filtered through a PTFE syringe filter and layered with hexanes to crystallize at −32 °C overnight. The solid was isolated by filtration through a glass filter frit inside the glovebox, washed with hexanes, and dried *in vacuo* overnight to give (S,S)-5 (0.0997 g, 75%) as a yellow solid. Occasionally subsequent recrystallizations from THF/hexanes were required to achieve the highest levels of purity. The catalyst rapidly decomposes upon exposure to air or water or if stored for an extended period of time at room temperature. **MP >200 °C.** $^1$H NMR (500 MHz, CDCl$_3$): δ 8.55 (s, 2H), 7.36 (d, $J$ = 2.6, 2H), 7.34 (d, $J$ = 2.6, 2H), 7.23 (m, 2H), 7.08 (m, 2H), 3.66 (m, 8H, THF), 3.50 (m, 2H), 2.70 (m, 2H), 2.14 (m, 2H), 1.87 (s, 6H), 1.77 (m, 8H, THF), 1.72 (s, 6H), 1.63 (m, 4H), 1.44 (s, 18H), 1.29 (s, 18H). $^{13}$C($^1$H) NMR (126 MHz, CDCl$_3$): δ 168.7, 159.8, 149.6, 140.9, 137.9, 137.3, 135.9, 135.0, 132.2, 129.8, 124.4, 123.9, 118.1, 69.9, 64.9, 34.6, 34.2, 31.8, 31.3, 28.2, 25.4, 23.7, 21.3, 20.0.
Isomerization of Epoxides to Ketones

2-Butanone (2b)

\[
\text{\begin{tikzpicture}
    \draw (-1,0) -- (1,0) -- (1,1) -- (-1,1) -- cycle;
\end{tikzpicture}}
\]

Following general procedure E, 1b (14.2 mg, 0.197 mmol), dodecane (9.0 mg, 0.053 mmol), 4 (4.0 mg, 0.0040 mmol, 2 mol %) in ether (0.8 mL) were used to produce the title compound. Quantitative GC analysis resulted in 95% yield.

3-Hexanone (2c)

\[
\text{\begin{tikzpicture}
    \draw (-1,0) -- (1,0) -- (1,1) -- (-1,1) -- cycle;
\end{tikzpicture}}
\]

Following general procedure E, 1c (23.8 mg, 0.238 mmol), dodecane (14.3 mg, 0.084 mmol), 4 (5.2 mg, 0.0051 mmol, 2.2 mol %) in ether (1 mL) were used to produce the title compound. Quantitative GC analysis resulted in 92% yield.

4-Octanone (2d)

\[
\text{\begin{tikzpicture}
    \draw (-1,0) -- (1,0) -- (1,1) -- (-1,1) -- cycle;
\end{tikzpicture}}
\]

Following general procedure F, 1d (255.9 mg, 1.996 mmol), 4 (40.5 mg, 0.0401 mmol, 2.0 mol %), and ether (8 mL) were used to give the title compound (221.9 mg, 87%) as a colorless oil. Analytical data for 2d matched those previously reported.\(^{18}\)\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 2.39 (overlapping t, \(J = 7.4, 2\)H), 2.37 (overlapping t, \(J = 7.3, 2\)H), 1.46–1.68 (m, 4H), 1.31 (sextet, \(J = 7.4, 2\)H), 0.91 (overlapping t, \(J = 7.4, 3\)H), 0.90 (overlapping t, \(J = 7.3, 3\)H). \(^{13}\)C\(^{1}\)H NMR (101 MHz, CDCl\(_3\)): \(\delta\) 211.4, 44.7, 42.6, 26.0, 22.4, 17.3, 13.9, 13.8.

3-Pentanone + 2-Pentanone (2e + 3e)

\[
\text{\begin{tikzpicture}
    \draw (-1,0) -- (1,0) -- (1,1) -- (-1,1) -- cycle;
\end{tikzpicture}} \quad \text{\begin{tikzpicture}
    \draw (-1,0) -- (1,0) -- (1,1) -- (-1,1) -- cycle;
\end{tikzpicture}}
\]

Following general procedure E, 1e (19.4 mg, 0.225 mmol), dodecane (13.8 mg, 0.0810 mmol), 4 (5.2 mg, 0.0051 mmol, 2.3 mol %) in ether (1 mL) were used to produce the title compound. Quantitative GC analysis resulted in 66% 3-pentanone, 12% 2-pentanone, for a total of 78% yield and a ratio of 5.5 : 1.

3-Hexanone + 2-Hexanone (2f + 3f)
Following general procedure E, 1f (18.8 mg, 0.188 mmol), dodecane (10.1 mg, 0.0593 mmol), 4 (4.1 mg, 0.0041 mmol, 2.2 mol %) in ether (0.8 mL) were used to produce the title compounds. Quantitative GC analysis resulted in 89% 3-hexanone, 9% 2-hexanone, for a total of 98% yield and a ratio of 10.7 : 1.

3-Heptanone + 2-Heptanone (2g + 3g)

Following general procedure E, 1g (23.6 mg, 0.207 mmol), dodecane (9.8 mg, 0.058 mmol), 4 (3.9 mg, 0.0039 mmol, 1.9 mol %) in ether (0.8 mL) were used to produce the title compounds. Quantitative GC analysis resulted in 92% 3-heptanone, 6% 2-heptanone, for a total of 98% yield and a ratio of 16.6 : 1.

3-Octanone (2a)

Following general procedure F, 1a (254.6 mg, 1.985 mmol), 4 (40.5 mg, 0.0401 mmol, 2.0%), and ether (8 ml) were used to give the title compound (197.9 mg, 78%) as a colorless oil. Analytical data for 2a matched those previously reported.\textsuperscript{19} \textsuperscript{1H NMR} (400 MHz, CDCl\textsubscript{3}): \(\delta\) 2.29–2.48 (m, 4H), 1.57 (quintet, \(J = 7.4\), 2H), 1.19–1.36 (m, 4H), 1.05 (t, \(J = 7.3\), 3H), 0.88 (t, \(J = 7.0\), 3H). \textsuperscript{13C\{\textsuperscript{1H}\} NMR} (101 MHz, CDCl\textsubscript{3}): \(\delta\) 211.6, 42.3, 35.7, 31.4, 23.6, 22.4, 13.8, 7.7.

3-Nonanone + 2-Nonanone (2h + 3h)

Following general procedure F, 1h (143.0 mg, 1.005 mmol), 4 (20.1 mg, 0.0199 mmol, 2.0 mol %), and ether (4 ml) were used to produce title compounds (117.9 mg, 82%) as a colorless oil. Analytical data for 2h and 3h matched those previously reported.\textsuperscript{20,21} Note that the Jun group from Yonsei University in South Korea reports a different \textsuperscript{13}C NMR for 3-nonanone, however their spectrum is missing the characteristic ethyl CH\textsubscript{3} at around 7 ppm.\textsuperscript{22} \textsuperscript{13C\{\textsuperscript{1H}\} NMR} (101 MHz, CDCl\textsubscript{3}): 3-nonanone: \(\delta\) 211.6, 42.3, 35.7, 31.5, 28.8, 23.8, 22.4, 13.9, 7.7. 2-Nonanone: 209.0, 43.8, 31.7, 29.8, 29.14, 29.08, 23.9, 22.6, 14.0. \textsuperscript{1H NMR} (400 MHz, CDCl\textsubscript{3}):
4-Octanone + 3-Octanone (2i + 3i)

Following general procedure F, 1i (256.3 mg, 1.999 mmol), 4 (40.5 mg, 0.0401 mmol, 2.0 mol %), and ether (8 ml) were used to give a 3.1 : 1 mixture of 4-octanone to 3-octanone (251.3 mg, 98%) as a colorless oil. Analytical data for 2i and 3i matched those previously been reported.\textsuperscript{18,19} \textsuperscript{13}C\textsuperscript{1}H NMR (101 MHz, CDCl\textsubscript{3}): 4-Octanone: δ 211.6, 44.8, 42.6, 26.0, 22.4, 17.4, 13.9, 13.8. 3-Octanone: δ 212.0, 42.4, 35.9, 31.5, 23.7, 22.5, 14.0, 7.9. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}):
1-Tert-butyldimethylsilyloxy-2-butanone (2k)

Following general procedure F, 1k (60.6 mg, 0.299 mmol), 4 (15.2 mg, 0.0150 mmol, 5.0%), and ether (3 ml) were used to give the title compound (59.1 mg, 98%) as a yellow oil. Analytical data for 2k matched those previously reported.\(^{23}\) \(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)): \(\delta\) 4.17 (s, 2H), 2.53 (q, \(J = 7.3\), 2H), 1.06 (t, \(J = 7.3\), 3H), 0.92 (s, 9H), 0.09 (s, 6H). \(^{13}\text{C}\{^1\text{H}\} \text{NMR}\) (101 MHz, CDCl\(_3\)): \(\delta\) 211.9, 69.2, 31.8, 25.9, 18.4, 7.3, −5.4.

6-Tert-butyldimethylsilyloxy-3-hexanone (2l)

Following general procedure F, 1l (38.6 mg, 0.168 mmol), 4 (6.1 mg, 0.0060 mmol, 3.5%), and ether (4 ml) were used to give the title compound (34.0 mg, 88%) as a colorless oil. Analytical data for 2l matched those previously reported.\(^{24}\) \(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)): \(\delta\) 3.61 (t, \(J = 6.1\), 2H), 2.48 (t, \(J = 7.3\), 2H), 2.44 (q, \(J = 7.3\), 2H), 1.78 (m, 2H), 1.05 (t, \(J = 7.3\), 3H), 0.88 (s, 9H), 0.03 (s, 6H). \(^{13}\text{C}\{^1\text{H}\} \text{NMR}\) (101 MHz, CDCl\(_3\)): \(\delta\) 211.7, 62.3, 38.8, 36.1, 27.0, 26.1, 18.4, 8.0, −5.2.

1-Phenylbutan-2-one (2m)
Following general procedure F, 1m (221.3 mg, 1.493 mmol), 4 (30.2 mg, 0.0299 mmol, 2.0 %), and ether (6 ml) were used to give the title compound (188.0 mg, 85%) as a colorless oil. Analytical data for 2m matched those previously reported.\textsuperscript{25} \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 7.14–7.39 (m, 5H), 3.69 (s, 2H), 2.48 (quartet, \( J = 7.3 \), 2H), 1.03 (t, \( J = 7.3 \), 3H). \textsuperscript{13}C\{\textsuperscript{1}H\} NMR (101 MHz, CDCl\textsubscript{3}): δ 208.9, 134.5, 129.4, 128.7, 126.9, 49.8, 35.2, 7.8.

1-(4-Methoxyphenyl)butan-2-one (2n)

Following general procedure F, 1n (179.8 mg, 1.009 mmol), 4 (20.3 mg, 0.0201 mmol, 2.0%), and ether (4 ml) were used to give the title compound (167.1 mg, 93%) as a colorless oil. Analytical data for 2n matched those previously been reported.\textsuperscript{26} \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 7.12 (m, 2H), 6.86 (m, 2H), 3.80 (s, 3H), 3.62 (s, 2H), 2.46 (q, \( J = 7.3 \), 2H), 1.02 (t, \( J = 7.3 \), 3H). \textsuperscript{13}C\{\textsuperscript{1}H\} NMR (101 MHz, CDCl\textsubscript{3}): δ 209.4, 158.6, 130.4, 126.6, 114.2, 55.3, 48.9, 35.1, 7.8.

1-Phenyl-2-propanone (3o)

Following general procedure F, 1o (135.0 mg, 1.006 mmol), 4 (20.2 mg, 0.0200 mmol, 2.0 mol %), and ether (4 ml) were used to give the title compound (112.3 mg, 83%) as a colorless oil. Analytical data for 3o matched those previously been reported.\textsuperscript{27} \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 7.31–7.37 (m, 2H), 7.25–7.30 (m, 1H), 7.19–7.22 (m, 2H), 3.70 (s, 2H), 2.16 (s, 3H). \textsuperscript{13}C\{\textsuperscript{1}H\} NMR (101 MHz, CDCl\textsubscript{3}): δ 206.4, 134.3, 129.5, 128.8, 127.1, 51.1, 29.3.
References

Copies of $^1$H and $^{13}$C[*$^1$H] NMR spectra

**rac-trans-2-Methyl-3-[4-(methoxyphenyl) methyl]-oxirane (1n), $^1$H NMR spectrum (400 MHz, CDCl$_3$)**

![NMR spectrum](image1)

$^{13}$C NMR spectrum (101 MHz, CDCl$_3$)

![NMR spectrum](image2)
rac-trans-2-Methyl-3-[(2-methylphenyl)methyl]-oxirane (1p), $^1$H NMR spectrum (400 MHz, CDCl$_3$)

$^{13}$C NMR spectrum (101 MHz, CDCl$_3$)
rac-trans-2-Methyl-3-[(3-methylphenyl)methyl]-oxirane (1q), $^1$H NMR spectrum (400 MHz, CDCl$_3$)

$^{13}$C NMR spectrum (101 MHz, CDCl$_3$)
**rac-trans-2-Methyl-3-[(4-methylphenyl)methyl]-oxirane (1r), \(^1\)H NMR spectrum (400 MHz, CDCl\(_3\))**

![NMR spectrum](image)

**\(^{13}\)C NMR spectrum (101 MHz, CDCl\(_3\))**

![NMR spectrum](image)
2,3-\textit{d}_2-\text{cis}-2\text{-Octene (SM1),}^1\text{H NMR spectrum} (400 MHz, CDCl$_3$)

$^1\text{C NMR spectrum}$ (101 MHz, CDCl$_3$)
(rel-R,R)-2,3-d_{2}-3-Chloro-2-octanol and 2,3-d_{2}-2-chloro-3-octanol (SM2), $^1$H NMR spectrum (400 MHz, CDCl$_3$)

$^{13}$C NMR spectrum (101 MHz, CDCl$_3$)
(rel-S,R)-2,3-d$_2$-2-Acetate-3-Chloro-2-octanol and 2,3-d$_2$-3-acetate-2-chloro-3-octanol (SM3), $^1$H NMR spectrum (400 MHz, CDCl$_3$)

$^{13}$C NMR spectrum (101 MHz, CDCl$_3$)
2,3-d$_2$-trans-2-Methyl-3-pentyloxirane (1a-d$_2$), $^1$H NMR spectrum (400 MHz, CDCl$_3$)

$^{13}$C NMR spectrum (101 MHz, CDCl$_3$)
4′,5-di(Tert-butyl)-2′,6′-dimethyl-[1,1′-biphenyl]-2-ol (SM4), $^1$H NMR spectrum (400 MHz, CDCl$_3$)

$^{13}$C NMR spectrum (101 MHz, CDCl$_3$)
2-Hydroxy-4',5-di(Tert-butyl)-2',6'-dimethyl-[1,1'-biphenyl]-3-carbaldehyde (SM5), $^1$H NMR spectrum (400 MHz, CDCl$_3$)

$^{13}$C NMR spectrum (101 MHz, CDCl$_3$)
3,3''-((1E,1'E)-((1S,2S)-Cyclohexane-1,2-diylbis(azanylylidene))bis(methanylylidene))-bis(4',5-di(tert-butyl)-2',6'-dimethyl-[1,1'-biphenyl]-2-ol) (SM6), $^1$H NMR spectrum (400 MHz, CDCl$_3$)

$^{13}$C NMR spectrum (101 MHz, CDCl$_3$)
3,3''-((1E,1'E)-((1S,2S)-Cyclohexane-1,2-diylbis(azanylylidene))bis(methanylylidene))-bis(4',5-di(tert-butyl)-2',6'-dimethyl-[1,1'-biphenyl]-2-olate)aluminum cobaltate (5), \(^1\)H NMR spectrum (400 MHz, CDCl\(_3\))

\[ S = \text{THF} \]

\[ \text{Co(CO)}_4^- \]

t-Bu

\[ \text{O} \]

\[ \text{Ar} \]

t-Bu

\[ \text{t-Bu} \]

\[ \text{t-Bu} \]

\[^{13}\text{C} NMR spectrum (101 MHz, CDCl}_3)\]
4-Octanone (2d), $^1$H NMR spectrum (400 MHz, CDCl$_3$)

$^{13}$C NMR spectrum (101 MHz, CDCl$_3$)
3-Octanone (2a), $^1$H NMR spectrum (400 MHz, CDCl$_3$)

$^{13}$C NMR spectrum (101 MHz, CDCl$_3$)
3-Nonanone + 2-Nonanone (2h + 3h, 14.3 : 1), $^1$H NMR spectrum (400 MHz, CDCl$_3$)

$^1$C NMR spectrum (101 MHz, CDCl$_3$)
4-Octanone + 3-Octanone (2i + 3i, 3.1 : 1), $^1$H NMR spectrum (400 MHz, CDCl$_3$)

$^1$C NMR spectrum (101 MHz, CDCl$_3$)
1-Tert-butyldimethylsilyloxy-2-butanone (2k), $^1$H NMR spectrum (400 MHz, CDCl$_3$)

$^1$C NMR spectrum (101 MHz, CDCl$_3$)

\[ \text{OTBS} \]
6-Tert-butylidemethylsilyloxy-3-hexanone (2l), $^1$H NMR spectrum (400 MHz, CDCl$_3$)

$^{13}$C NMR spectrum (101 MHz, CDCl$_3$)
1-Phenylbutan-2-one (2m), $^1$H NMR spectrum (400 MHz, CDCl$_3$)

$^1$C NMR spectrum (101 MHz, CDCl$_3$)
1-(4-Methoxyphenyl)butan-2-one (2n), $^1$H NMR spectrum (400 MHz, CDCl$_3$)

$^{13}$C NMR spectrum (101 MHz, CDCl$_3$)
1-Phenyl-2-propanone (3o), $^1$H NMR spectrum (400 MHz, CDCl$_3$)

$^{13}$C NMR spectrum (101 MHz, CDCl$_3$)