Supporting Information

Regioselective Carbonylation of 2,2-Disubstituted Epoxides: An Alternative Route to Ketone-Based Aldol Products

Aran K. Hubbell, Anne M. LaPointe, Jessica R. Lamb, and Geoffrey W. Coates*

Department of Chemistry and Chemical Biology, Baker Laboratory, Cornell University, Ithaca, New York 14853-1301

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A. General. 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. $^1$H NMR and $^{13}$C($^1$H) NMR spectra were recorded on a Bruker 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)). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sep = septet, m = multiplet), integration, and coupling constants (Hz). Deuterated chloroform was purchased from Cambridge Isotope Laboratories and stored over 3 Å molecular sieves. HRMS analyses were performed on a Thermo Scientific Exactive Orbitrap MS system with an Ion Sense DART ion source. Enantiomeric ratios of isolated material were determined by chiral HPLC using a SHIMADZU system with a CHIRALPAK® OD column or chiral GC using a Hewlett Packard 6890 gas chromatograph equipped with an Astec CHIRALDEX A-TA and a Supelco β-Dex 225 column as well as a flame ionization detector, in comparison with authentic racemic materials. Helium (Airgas, Ultra High Purity grade) was used as the carrier gas. Optical rotations were measured on a Perkin-Elmer polarimeter in CHCl$_3$. The kinetics experiments were conducted on a Freeslate Core Module 3™ (CM3) robotic platform located under a N$_2$ atmosphere inside an MBraun drybox. The experiment was designed and executed using Library Studio™ and Automation Studio™ software, respectively. All solutions were dispensed robotically using a syringe dispense. These reactions were performed in a Freeslate HiP high pressure reactor containing 96 x 1 mL glass vials. For these experiments, solvent was removed in the glovebox using a vacuum centrifuge fitted with an external liquid nitrogen trap. Flash column chromatography was performed with silica gel (particle size 40–64 µm, 230–400 mesh) using mixtures of hexanes and diethyl ether. All work-up and purification procedures were carried out with reagent grade solvents (purchased from Fisher) in air.

B. Sources of Solvents, Reagents, and Catalysts:

Acetonitrile was passed through two columns packed with neutral alumina and copper(II) oxide and degassed by three freeze-pump-thaw cycles before being stored over 3 Å molecular sieves. Azidotrimethylsilane was purchased from Sigma-Aldrich and used as received. Calcium hydride was purchased from Strem and crushed with a mortar and pestle prior to use. Carbon monoxide was purchased from Matheson (research quality/>99.99% min purity) and used as received. 2-(Chloromethyl)-2-methyloxirane (2p) was purchased from Combi-Blocks, dried over calcium hydride for 24 h, and degassed via three freeze-pump-thaw cycles prior to use. 3-Chloroperbenzoic acid was purchased from Sigma-Aldrich (≤77%) and used as received. Cyclohexane was purchased from Fischer Chemical and used as received. Deuterated chloroform was purchased from Cambridge Isotope Laboratories and stored over activated 3 Å molecular sieves. Decolorizing carbon was purchased from Fischer Chemical and used as received. Dichloromethane was purchased from Fischer Chemical and sparged vigorously with nitrogen for 40 minutes before passing through two packed columns of neutral alumina under nitrogen pressure. Later it was degassed via three freeze-pump-thaw cycles prior to use. Dicobalt octacarbonyl was purchased from Strem and stored at −30 °C prior to use. Diethyl ether was purchased from Fischer Chemical, dried over calcium hydride for 24 h, and degassed via three freeze-pump-thaw cycles prior to use. Diethylaluminum chloride was purchased from Sigma-Aldrich and diluted to make a 1.0 M
solution in dry hexanes prior to use. 

**Diisopropyl ether** was purchased from TCI, dried over calcium hydride for 24 h, and degassed via three freeze-pump-thaw cycles prior to use. 

**2,3-Dimethyl-1-butene** was purchased from TCI and used as received. 

**Dimethyl sulfoxide** was purchased from Fisher Chemical and used as received. 

**2,5-Dimethyltetrahydrofuran** was purchased from Lancaster Synthesis, dried over calcium hydride for 24 h, and degassed via three freeze-pump-thaw cycles prior to use. 

**1,4-Dioxane** was purchased from Sigma-Aldrich, dried over 3 Å molecular sieves for 24 h, syringe filtered, and sparged with nitrogen for 30 minutes prior to use. 

**2-Ethyl-1-butene** was purchased from TCI and used as received. 

**Hexamethyldisiloxane** was purchased from Alfa Aesar, dried over 3 Å molecular sieves for 24 h, and degassed via three freeze-pump-thaw cycles prior to use. 

**Hexanes** was purchased from Fischer Chemical and sparged with nitrogen for 40 minutes before passing through two packed columns of neutral alumina and copper(II) oxide under nitrogen pressure. 

**Imidazole** was purchased from Sigma-Aldrich and used as received. 

**Isobutylene oxide (2a)** was purchased from TCI, dried over calcium hydride for 24 h, and degassed via three freeze-pump-thaw cycles prior to use. 

**2,6-Lutidine** was purchased from Sigma-Aldrich and used as received. 

**Magnesium sulfate** was purchased from Fisher Chemical and used as received. 

**Methallylcyclopentane** was purchased from Alfa Aesar and used as received. 

**Methallyl phenyl ether** was purchased from Lancaster Synthesis and used as received. 

**2-Methyl-1-butene** was purchased from TCI and used as received. 

**3-Methyl-3-buten-1-ol** was purchased from Lancaster Synthesis and used as received. 

**Methylenecyclohexane** was purchased from Sigma-Aldrich and used as received. 

**2-Methyl-1-pentene** was purchased from TCI and used as received. 

**2-Methyl-1-phenyl-1-propene** was purchased from Alfa Aesar and used as received. 

**2-Methyl-2-propen-1-ol** was purchased from Sigma-Aldrich and used as received. 

**2-Methyl-1-heptene** was purchased from TCI and used as received. 

**Methyl methacrylate** was purchased from Sigma-Aldrich and used as received. 

**2-Methyl-1-undecene** was purchased from Sigma-Aldrich and used as received. 

**Octaethylporphyrin** was purchased from Frontier Scientific and used as received. 

**4-Phenyl-2-butanone** was purchased from TCI and used as received. 

**Potassium tert-butoxide** was purchased from Sigma Aldrich and used as received. 

**2-Propanol** was purchased from Fischer Chemical and dried over 3 Å molecular sieves for 24 h prior to use. 

**Sodium bicarbonate** was purchased from Macron Fine Chemicals and diluted to make a saturated solution in deionized water prior to use. 

**Sodium hydroxide** was purchased from J. T. Baker, crushed, and dried under vacuum prior to use. 

**Sodium methoxide solution in methanol (0.5 M)** was purchased from Sigma-Aldrich and used as received. 

**Sodium thiosulfate** was purchased from Alfa Aesar and diluted to make a saturated solution in deionized water prior to use. 

**Tert-butylidimethylchlorosilane** was purchased from TCI and used as received. 

**Tert-butylidimethylsilyl trifluoromethanesulfonate** was purchased from Alfa Aesar and used as
Tert-butyl methacrylate was purchased from TCI and used as received.
*Tert-butyl 1-oxa-6-azaspiro[2.5]octane-6-carboxylate (2I)* was purchased from Combi-Blocks and used as received.
*Tetrahydrofuran* was purchased from Fisher Chemical and sparged with nitrogen for 40 minutes before passing through two packed columns of neutral alumina and a third column packed with activated 4Å molecular sieves under nitrogen pressure.
*Toluene* was purchased from Fisher Chemical and sparged with nitrogen for 40 minutes before passing through two packed columns of neutral alumina and copper(II) oxide under nitrogen pressure.
2,3,3-Trimethyl-1-butene was purchased from Sigma Aldrich and used as received.
Trimethylsulfoxonium iodide was purchased from TCI and used as received.

Compounds prepared according to literature procedures:

\[ N,N'\text{-Bis(3,5-di-tert-butylsalicylidene)-1,2-phenylenediaminoaluminum cobalt tetracarbonyl}\]
\[ ((\text{salph})\text{Al(THF)}_2)^+\text{[Co(CO)}_4^-\text{]} (\text{1a})^1 \]

Bis(tetrahydrofuran)-meso-tetraphenylporphyrinato aluminum tetracarbonyl cobaltate,
\[ ([\text{TPP}\text{Al(THF)}_2]^+\text{[Co(CO)}_4^-\text{]} (\text{1b})^2 \]

Bis(tetrahydrofuran)-meso-tetra(4-chlorophenyl)porphyrinato aluminum tetracarbonyl cobaltate,
\[ ([4\text{-ClTPP}\text{Al(THF)}_2]^+\text{[Co(CO)}_4^-\text{]} (\text{1c})^2 \]

Bis(tetrahydrofuran)-meso-tetra(4-methoxyphenyl)porphyrinato aluminum tetracarbonyl cobaltate,
\[ ([4\text{-OMeTPP}\text{Al(THF)}_2]^+\text{[Co(CO)}_4^-\text{]} (\text{1d})^2 \]

Bis(tetrahydrofuran)-meso-tetra(2,4,6-trimethylphenyl)porphyrinato aluminum tetracarbonyl cobaltate,
\[ ([2,4,6\text{-trimethylTPP}\text{Al(THF)}_2]^+\text{[Co(CO)}_4^-\text{]} (\text{1e})^2 \]

Bis(tetrahydrofuran)-octaethylporphyrinato aluminum tetracarbonyl cobaltate,
\[ ([\text{OEP}\text{Al(THF)}_2]^+\text{[Co(CO)}_4^-\text{]} (\text{1f})^2 \]

*Tert-butyldimethyl((2-methylallyl)oxy)silane (S1)^3*
*Tert-butyldimethyl((3-methylbut-3-en-1-yl)oxy)silane (S2)^3*
Methyl 2-methyloxirane-2-carboxylate (2s)^4
C. Control Experiments

\[
\begin{align*}
\text{Me} & \quad \text{O} \\
\text{Me} & \quad \text{Me}
\end{align*}
\]

\[
\text{2a}
\]

\[
\begin{align*}
\overset{\text{catalyst}}{\text{Me}} & \quad \overset{\text{O}}{\text{Me}} \\
\overset{\text{CO (900 psi), 0.5 M Pr}_2\text{O}}{\text{22 °C, 2 h}} & \quad \overset{\text{Me}}{\text{Me}} \\
\overset{\text{C}}{\text{O}} & \quad \overset{\text{O}}{\text{O}} \\
\overset{\text{Me}}{\text{Me}} & \quad \overset{\text{Me}}{\text{Me}}
\end{align*}
\]

\[
\text{3a} + \quad \text{4a}
\]

| entry | catalyst | mol % catalyst | conv. (%)$^a$ |
|-------|----------|----------------|---------------|
| 1     | If       | 1.0            | 45            |
| 2     | NaCo(CO)$_4$ | 1.0          | <1            |
| 3     | --       | 0              | <1            |

$^a$Determined by $^1$H NMR analysis of crude reaction mixture.
D. Mechanistic Studies by $^1$H NMR Analysis: Order in Carbon Monoxide

In a glovebox, 1f (1.0 mol %, 3.5 mg, 0.0040 mmol) was weighed into five individual 4 mL vials equipped with Teflon-coated magnetic stir bars and septa caps. A separate 8 mL glass vial equipped with a Teflon-coated magnetic stir bar was charged with 2a (186 mg, 2.60 mmol) and $^3$Pr$_2$O (0.5 M, 5.2 mL). 0.8 mL of the stock solution was added to each of the five vials containing 1f. Each septum cap was pierced with a needle, and the vials were placed in a custom-made six-well high-pressure reactor. Each well was exposed to a different pressure of carbon monoxide (200, 350, 500, 700, and 900 psi). To work up these reactions, the reactor was carefully vented in a well-ventilated hood on emergency exhaust. A portion of each reaction was run through a decolorizing carbon plug with deuterated chloroform into an NMR tube to remove catalyst before analyzing by $^1$H NMR spectroscopy. The conversion of 2a to 3a was plotted as a function of carbon monoxide pressure ($P_{CO}$). Assuming that [CO] is proportional to $P_{CO}$, this trend is consistent with a near zero-order rate dependence on $P_{CO}$.

![Chemical structure](image)

| entry | $P_{CO}$ (psi) | conv. (%)$^a$ | ratio 3a:4a$^a$ |
|-------|----------------|---------------|----------------|
| 1     | 200            | 35            | >99:1          |
| 2     | 350            | 39            | >99:1          |
| 3     | 500            | 41            | 99:1           |
| 4     | 700            | 47            | 99:1           |
| 5     | 900            | 45            | 99:1           |

$^a$Determined by $^1$H NMR analysis of crude reaction mixture.

**Rate Dependence on $P_{CO}$**

![Graph](image)

$y = 0.0164x + 32.485$

$R^2 = 0.83208$
E. Mechanistic Studies by \(^1\)H NMR Analysis: Order in Catalyst

These kinetics experiments were conducted on a Freeslate Core Module 3™ (CM3) robotic platform under a N\(_2\) atmosphere in an MBraun drybox. These reactions were run in triplicate and performed in a Freeslate HiP high pressure reactor containing 96 x 1 mL glass vials. 100, 200, 300, 400, and 500 µl of a stock solution of 1f in Et\(_2\)O (10 mM) was dispensed robotically into individual 1 mL shell vials containing disposable stir bars. Volatiles were then removed from the vials using a Speedvac vacuum centrifuge (22 °C, 30 minutes) fitted with an external liquid nitrogen trap. The vials were transferred to the Freeslate 96-well HiP reactor. The temperature of the reactor was set to −20 °C, and the stir rate was set to 300 rpm. A stock solution of epoxide 2a (1.0 eq., 0.5 M) and an internal standard (hexamethyldisiloxane, 0.3 eq.) in diisopropyl ether (\(^1\)Pr\(_2\)O) was made and 200 µl was dispensed robotically into vials containing catalyst. The reactor was then sealed, brought out of the glovebox, and pressurized with 250 psi of carbon monoxide. The 15 vials were stopped after 2 h of reaction time by carefully venting the reactor in a well-ventilated hood on emergency exhaust. A portion of each reaction was run through a decolorizing carbon plug with deuterated chloroform into an NMR tube to remove catalyst before analyzing by \(^1\)H NMR spectroscopy. The concentrations of lactone product were plotted as a function of initial catalyst concentration. The linear trend indicates that the reaction is first order in catalyst.

![Rate Dependence on [1f] in \(^1\)Pr\(_2\)O](image-url)
Mechanistic Studies by $^1$H NMR Analysis: Order in Epoxide

These kinetics experiments were conducted on a Freeslate Core Module 3$^{\text{TM}}$ (CM3) robotic platform under a N$_2$ atmosphere in an MBraun drybox. These reactions were run in triplicate and performed in a Freeslate HiP high pressure reactor containing 96 x 1 mL glass vials. 300 µl of a stock solution of 1f in Et$_2$O (10 mM) was dispensed robotically into individual 1 mL shell vials containing disposable stir bars. Volatiles were then removed from the vials using a Speedvac vacuum centrifuge (22 °C, 30 minutes) fitted with an external liquid nitrogen trap. The vials were transferred to the Freeslate 96-well HiP reactor. The temperature of the reactor was set to −20 °C, and the stir rate was set to 300 rpm. 180, 160, 120, 80, 40, and 0 µl of Pr$_2$O were dispensed into the six vials. A stock solution of 2a (1.0 M) and an internal standard (hexamethyldisiloxane, 0.3 eq.) in Pr$_2$O was made. 20, 40, 80, 120, 160, and 200 µl of this stock solution were dispensed into each set of six vials containing 1f in Pr$_2$O to generate 18 vials with 200 µl total volume (0.1, 0.2, 0.4, 0.6, 0.8, and 1.0 M). The reactor was then sealed, brought out of the glovebox, and pressurized with 250 psi of carbon monoxide. The 18 vials were stopped after 0.25 h of reaction time by carefully venting the reactor in a well-ventilated hood on emergency exhaust. A portion of each reaction was run through a decolorizing carbon plug with deuterated chloroform into an NMR tube to remove catalyst before analyzing by $^1$H NMR spectroscopy. The concentrations of lactone product were plotted as a function of initial epoxide concentration. The shallow slope indicates that the reaction is zeroth order in epoxide using Pr$_2$O as a solvent. These reactions were repeated in THF (for 2 h), generating a linear trend which indicates that the reaction is first order in epoxide using THF as a solvent.

Rate Dependence on [IBO] in THF and Pr$_2$O

![Graph showing rate dependence on [IBO] in THF and Pr$_2$O](image-url)
Representative Procedures

G. General Procedure A: Epoxidation of alkenes using \textit{m}CPBA (2b–2k, 2m–2o, 2q–2r).

\[
\begin{align*}
R^1 & \quad 1.2 \text{ eq. } m\text{CPBA} \quad 0.5 \text{ M DCM, } 0\text{–}22 ^\circ C \\
R^2 & \quad \text{ R}^1 \quad \text{ R}^2
\end{align*}
\]

Under ambient atmosphere, 1.2 eq. of \textit{m}CPBA (Aldrich, \(\leq 77\%\)) was added slowly to a stirring solution of a 1,1-disubstituted alkene in benchtop DCM (0.5 M) at 0 °C to avoid boiling. The resulting mixture was stirred at room temperature until complete consumption of starting material was observed by \(^1\text{H} \text{NMR}\) of the crude reaction mixture. Aqueous Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} was added to destroy any excess \textit{m}CPBA, and the reaction mixture stirred for an additional hour before filtering through celite. The aqueous phase was extracted with DCM (3x), and organics were combined and washed with NaHCO\textsubscript{3} (3x), dried with MgSO\textsubscript{4}, filtered, and concentrated.

H. General Procedure B: Epoxidation of methacrylates using \textit{m}CPBA (2s–2t).

\[
\begin{align*}
R^1 & \quad 1.5 \text{ eq. } m\text{CPBA} \quad 0.5 \text{ M cyclohexane, } 0\text{–}90 ^\circ C \\
R^2 & \quad \text{ R}^1 \quad \text{ R}^2
\end{align*}
\]

A literature procedure was adapted for the epoxidation of methacrylate-type alkenes. Under ambient atmosphere, 1.5 eq. of \textit{m}CPBA (Aldrich, \(\leq 77\%\)) was added slowly to a solution of a 1,1-disubstituted alkene in benchtop cyclohexane (0.5 M) at 0 °C to avoid boiling. The resulting mixture was stirred at 90 °C until complete consumption of starting material was observed by \(^1\text{H} \text{NMR}\) of the crude reaction mixture. Aqueous Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} was added to destroy any excess \textit{m}CPBA, and the reaction mixture stirred for an additional hour before filtering through celite. The filtrate was concentrated to 1/3 its original volume and filtered again to remove solids. The organic layer was washed with NaHCO\textsubscript{3} (3x) and H\textsubscript{2}O (3x) before being dried with MgSO\textsubscript{4}, filtered, and concentrated.

I. General Procedure C: Carbonylation of 2,2-disubstituted epoxides (3a–3t).

\[
\begin{align*}
R^1 & \quad \text{guide} \quad \text{guide} \\
R^2 & \quad \text{ CO (900 psi), 0.5 M Solvent} \\
\end{align*}
\]

In a glovebox, a 4 mL glass vial equipped with a Teflon-coated magnetic stir bar and septum cap was charged with catalyst and solvent (0.5 M with respect to epoxide). The septum was then pierced with a needle, and the vial was placed in a custom-made six-well high-pressure reactor. The appropriate epoxide was then added dropwise to the vial by weight. The reactor was subsequently sealed, taken out of the glovebox, placed in a well-ventilated hood, and pressurized with carbon monoxide (900 psi). The closed reactor stirred for the time indicated. To work up these reactions, the reactor was carefully vented in a well-ventilated hood on emergency exhaust, and the crude reaction mixture was filtered through a decolorizing carbon plug made from a pipette and a glass microfiber filter to remove catalyst. The solution was concentrated and loaded with hexanes onto a column with increasing eluent polarity (100% hexanes, 19:1 hexanes:Et\textsubscript{2}O, 9:1 hexanes:Et\textsubscript{2}O, 3:1 hexanes:Et\textsubscript{2}O). Both epoxide and lactone can be visualized using KMnO\textsubscript{4}, cerium ammonium molybdate (CAM/Hanessian’s Stain), and/or \(p\)-anisaldehyde TLC stains.
J. General Procedure D: Ring-opening of β,β-disubstituted β-lactones (6f, 6m, 6n, 6o, 6r, and 6t).

```
R
O
R

1.3 eq. NaOMe in MeOH
0.5 M THF, 22 °C, 1 min

OH
R
7
R
O
OMe

```
Purified lactone generated via general procedure C was diluted in THF (0.5 M) in a 20 mL vial before adding 1.3 eq. of NaOMe in MeOH. The mixture was stirred for 1 min before it was filtered through a silica gel plug, which was washed thoroughly with diethyl ether. The solution was concentrated to yield the aldol product. No column chromatography is necessary for purification.

K. General Procedure E: Alternative one-pot carbonylation/ring-opening method (6f, 6m, 6n, 6o, 6r, and 6t).

After the six-well high-pressure reactor was vented (see general procedure C) and before filtering with decolorizing carbon, the vial of crude lactone was charged with 1.3 eq. of 0.5 M NaOMe in MeOH and allowed to stir for 1 min. The crude mixture was then filtered through a decolorizing carbon pipette plug to remove the catalyst. After washing the plug with diethyl ether, the solution was concentrated and loaded with hexanes onto a column with increasing eluent polarity (100% hexanes, 19:1 hexanes:Et₂O, 9:1 hexanes:Et₂O). All aldol products can be visualized using KMnO₄, cerium ammonium molybdate (CAM/Hanessian’s Stain), and/or p-anisaldehyde TLC stains.

```
Me

R
O

1) catalyst 1b or 1f
CO (900 psi)

2) NaOMe, MeOH,
1 min

OH
R
7
R
O
OMe

```

| entry | β-lactone | R         | product | yield 6 (%)<sup>a</sup> |
|-------|-----------|-----------|---------|-------------------------|
| 1     | 3f        | "Pent"    | 6f      | 25                      |
| 2     | 3m        | Bn        | 6m      | 40                      |
| 3     | 3n        | CH₂Bn     | 6n      | 38                      |
| 4     | 3o        | CH₂OPh    | 6o      | 33                      |
| 5     | 3r        | CH₂CH₂OTBS| 6r      | 72                      |
| 6     | 3t        | COO'Bu    | 6t      | 54                      |

<sup>a</sup>Isolated yield after one-pot, two-step carbonylation/ring-opening reaction.
L. $^1$H, $^{13}$C NMR, and HRMS of Epoxides, β-Lactones, and Ketone-Aldol Products. All compounds are previously unreported or reported without analytical data unless otherwise stated.

**Epoxides**

**2-Ethyl-2-methyloxirane (2b)**

Following general procedure A, 2b was produced as a colorless oil (638 mg, 8% due to volatility). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 2.62 (d, 1H, $J = 4.9$ Hz), 2.57 (d, 1H, $J = 4.9$ Hz), 1.66–1.51 (m, 2H), 1.30 (s, 3H), 0.95 (t, 3H, $J = 7.6$ Hz); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 57.91, 53.75, 29.66, 20.72, 9.41; HRMS (DART): Calcd for C$_5$H$_{10}$O [M+H]$^+$: 87.08044. Found: 87.08085.

**2-Propyl-2-methyloxirane (2c)**

Following general procedure A, 2c was produced as a colorless oil (611 mg, 9% due to volatility). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 2.61 (d, 1H, $J = 4.9$ Hz), 2.57 (d, 1H, $J = 4.9$ Hz), 1.61–1.40 (m, 4H), 1.30 (s, 3H), 0.93 (t, 3H, $J = 7.3$ Hz); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 57.11, 54.09, 39.01, 20.99, 18.71, 14.29; HRMS (DART): Calcd for C$_6$H$_{12}$O [M+H]$^+$: 101.09609. Found: 101.09638.

**2-Isopropyl-2-methyloxirane (2d)**

Following general procedure A, 2d was produced as a colorless oil (6.77 g, 49%). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 2.60 (d, 1H, $J = 4.9$ Hz), 2.55 (d, 1H, $J = 4.9$ Hz), 1.50 (sep, 1H, $J = 6.9$ Hz), 1.23 (s, 3H), 0.99 (d, 3H, $J = 6.9$ Hz), 0.93 (d, 3H, $J = 7.0$ Hz); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 60.53, 53.87, 34.48, 18.65, 18.16, 17.15; HRMS (DART): Calcd for C$_6$H$_{12}$O [M+H]$^+$: 101.09609. Found: 101.09647.

**2-(Tert-butyl)-2-methyloxirane (2e)**

Following general procedure A, 2e was produced as a colorless oil (1.04 g, 18%). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 2.80 (d, 1H, $J = 4.7$ Hz), 2.43 (d, 1H, $J = 4.7$ Hz), 1.29 (s, 3H), 0.94 (s, 9H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 61.94, 51.89, 33.42, 26.12, 18.69; HRMS (DART): Calcd for C$_7$H$_{14}$O [M+H]$^+$: 115.07536. Found: 115.07568.
2-Methyl-2-pentyloxirane (2f)

Following general procedure A, 2f was produced as a colorless oil (3.23 g, 79%). Analytical data match literature values. \( ^1 \)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) 2.60 (d, 1H, \( J = 4.9 \) Hz), 2.57 (d, 1H, \( J = 4.9 \) Hz), 1.62–1.56 (m, 1H), 1.50–1.45 (m, 1H), 1.42–1.26 (m, 9H), 0.89 (t, 3H, \( J = 6.8 \) Hz); \( ^{13} \)C NMR (125 MHz, CDCl\(_3\)): \( \delta \) 57.25, 54.12, 36.88, 32.01, 25.09, 22.75, 22.05, 14.15; HRMS (DART): Calcd for C\(_8\)H\(_{16}\)O [M+H\(^+\)]: 129.12739. Found: 129.12744.

2-Hexyl-2-methyloxirane (2g)

Following general procedure A, 2g was produced as a colorless oil (3.01 g, 57%). \( ^1 \)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) 2.60 (d, 1H, \( J = 5.0 \) Hz), 2.57 (d, 1H, \( J = 4.9 \) Hz), 1.62–1.55 (m, 1H), 1.51–1.45 (m, 1H), 1.41–1.35 (m, 2H), 1.30–1.27 (m, 9H), 0.90–0.87 (m, 3H); \( ^{13} \)C NMR (125 MHz, CDCl\(_3\)): \( \delta \) 57.25, 54.12, 36.92, 31.94, 29.49, 25.38, 22.72, 21.05, 14.22; HRMS (DART): Calcd for C\(_9\)H\(_{18}\)O [M+H\(^+\)]: 143.14304. Found: 143.14320.

2-Methyl-2-nonyloxirane (2h)

Following general procedure A, 2h was produced as a colorless oil (1.50 g, 73%). \( ^1 \)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) 2.60 (d, 1H, \( J = 5.0 \) Hz), 2.57 (d, 1H, \( J = 4.9 \) Hz), 1.62–1.55 (m, 1H), 1.50–1.45 (m, 1H), 1.41–1.35 (m, 2H), 1.32–1.26 (m, 14H), 0.88 (t, 3H, \( J = 6.9 \) Hz); \( ^{13} \)C NMR (125 MHz, CDCl\(_3\)): \( \delta \) 57.26, 54.13, 36.92, 32.04, 29.83, 29.74, 29.68, 29.46, 25.43, 22.83, 21.06, 14.27; HRMS (DART): Calcd for C\(_{12}\)H\(_{24}\)O [M+H\(^+\)]: 185.18999. Found: 185.19074.

2-(Cyclopentylmethyl)-2-methyloxirane (2i)

Following general procedure A, 2i was produced as a colorless oil (2.46 g, 68%). \( ^1 \)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) 2.60 (d, 1H, \( J = 5.0 \) Hz), 2.57 (d, 1H, \( J = 4.9 \) Hz), 1.96–1.87 (m, 1H), 1.85–1.76 (m, 2H), 1.71 (dd, 1H, \( J = 6.7, 13.8 \) Hz), 1.66–1.57 (m, 2H), 1.57–1.47 (m, 2H), 1.43 (dd, 1H, \( J = 8.0, 13.8 \) Hz), 1.32 (s, 3H), 1.19–1.06 (m, 2H); \( ^{13} \)C NMR (125 MHz, CDCl\(_3\)): \( \delta \) 57.01, 54.33, 43.05, 37.24, 33.36, 33.02, 25.19, 25.03, 21.32; HRMS (DART): Calcd for C\(_9\)H\(_{18}\)O [M+H\(^+\)]: 141.12739. Found: 141.12760.
2,2-Diethyloxirane (2j)

Following general procedure A, 2j was produced as a colorless oil (4.37 g, 36%). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 2.58 (s, 2H), 1.69–1.53 (m, 4H), 0.92 (t, 6H, $J = 7.6$ Hz); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 61.01, 51.97, 26.84, 9.04; HRMS (DART): Calcd for C$_6$H$_{13}$O $[\text{M+H}]^+: 101.09609$. Found: 101.09649.

1-Oxaspiro[2.5]octane (2k)

Following general procedure A, 2k was produced as a colorless oil (1.17 g, 20%). Analytical data match literature values.$^7$ $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 2.59 (s, 2H), 1.76–1.71 (m, 2H), 1.60–1.48 (m, 8H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 59.19, 54.66, 33.81, 25.42, 25.06; HRMS (DART): Calcd for C$_7$H$_{12}$O $[\text{M+H}]^+: 113.09609$. Found: 113.09638.

2-Benzyl-2-methyloxirane (2m)

Following general procedure A, 2m was produced as a colorless oil (4.92 g, 99%). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.35–7.31 (m, 2H), 7.28–7.24 (m, 3H), 2.92 (d, 1H, $J = 14.2$ Hz), 2.85 (d, 1H, $J = 14.2$ Hz), 2.68 (d, 1H, $J = 4.9$ Hz), 2.64 (d, 1H, $J = 4.9$ Hz), 1.31 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 137.31, 129.65, 128.42, 126.66, 57.35, 53.41, 43.19, 20.98; HRMS (DART): Calcd for C$_{10}$H$_{12}$O $[\text{M+H}]^+: 149.09609$. Found: 149.09615.

(R)-2-Methyl-2-phenethyloxirane (R-2n)

The title compound was synthesized using a procedure adapted from the literature.$^8$ To a solution of KOt-Bu (1.00 eq., 7.10 g, 63.3 mmol) in DMSO (70 mL, 1.0 M) at 22 °C was added trimethylsulfoxonium iodide (1.10 eq., 15.3 g, 69.6 mmol), and the solution was allowed to stir for 30 min. A solution of 4-phenyl-2-butanone (1.00 eq., 63.3 mmol, 9.40 g) in DMSO (16 mL, 4.0 M) was added and allowed to stir until complete consumption of starting material was observed by $^1$H NMR (approximately 30 min). The reaction mixture was diluted with ethyl acetate and water. The layers were separated, and the aqueous layer was extracted with ethyl acetate (3x). Combined organic layers were washed with brine (1x), dried with MgSO$_4$, filtered, and concentrated. The crude product was loaded with hexanes onto a column with increasing eluent polarity (100% hexanes, 19:1 hexanes:Et$_2$O, 9:1 hexanes:Et$_2$O), and 2n was produced as a colorless oil (7.34 g, 71%). A literature kinetic resolution procedure$^9$ was used to obtain (R)-2n in >99:1 e.r. (1.54 g, 26%, maximum yield = 40%) using 0.6 eq. of both $^1$PrOH and TMSN$_3$. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.30–7.27 (m, 2H), 7.21–7.18 (m, 3H), 2.77–2.67 (m, 2H), 2.61 (d, 1H, $J = 4.9$ Hz), 2.58 (d, 1H, $J = 4.8$ Hz), 1.96–1.90 (m, 1H), 1.87–1.81 (m, 1H), 1.38 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 141.74, 128.57, 128.41, 126.10, 56.85, 54.08, 38.71, 31.59, 21.19; HRMS
(DART): Calcd for C$_{11}$H$_{14}$O [M+H]$^+$: 163.11174. Found: 163.11166; specific rotation: [α]$_D^{20}$ $-$ 4.07 (c = 0.54, CHCl$_3$) for an enantiomerically enriched sample of >99:1 e.r. Enantiomeric purity (>99:1) was determined by HPLC analysis in comparison with authentic racemic material. CHIRALPAK® OD column, 90% hexanes, 10% iPrOH, 1.0 mL/min, 254 nm.
2-Methyl-2-(phenoxy)methyloxirane (2o)

Following general procedure A, 2o was produced as a colorless oil (2.69 g, 26%). $^1$H NMR (500 MHz, CDCl$_3$): δ 7.30–7.27 (m, 2H), 6.98–6.95 (m, 1H), 6.93–6.91 (m, 2H), 4.02 (d, 1H, $J$ = 10.4 Hz), 3.96 (d, 1H, $J$ = 10.9 Hz), 2.88 (d, 1H, $J$ = 4.8 Hz), 2.74 (d, 1H, $J$ = 4.8 Hz), 1.49 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 158.75, 129.63, 121.29, 114.78, 71.60, 55.70, 52.24, 18.67; HRMS (DART): Calcd for C$_{10}$H$_{12}$O$_2$ [M+H$^+$]: 159.10157. Found: 159.10151.

Tert-butyldimethyl((2-methyloxiran-2-yl)methoxy)silane (2q)

Following general procedure A using S1, 2q was produced as a colorless oil (7.47 g, 85%). $^1$H NMR (500 MHz, CDCl$_3$): δ 3.65 (d, 1H, $J$ = 11.3 Hz), 3.60 (d, 1H, $J$ = 11.4 Hz), 2.74 (d, 1H, $J$ = 5.0 Hz), 2.60 (d, 1H, $J$ = 5.0 Hz), 1.34 (s, 3H), 0.90 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 66.71, 57.32, 51.81, 26.02, 18.51, 18.25, −5.23; HRMS (DART): Calcd for C$_{10}$H$_{22}$O$_2$Si [M+H$^+$]: 203.14618. Found: 203.14613.

Tert-butyldimethyl(2-(2-methyloxiran-2-yl)ethoxy)silane (R-2r)

Following general procedure A using S2, 2r was produced as a colorless oil (17.7g, 89%). A literature kinetic resolution procedure$^{10}$ was used to obtain (R)-2r in >99:1 e.r. (729 mg, 18%, maximum yield = 40%) using 0.6 eq. of both $^3$PrOH and TMSN$_3$. $^1$H NMR (500 MHz, CDCl$_3$): δ 3.76–3.69 (m, 2H), 2.69 (d, 1H, $J$ = 5.0 Hz), 2.58 (d, 1H, $J$ = 5.0 Hz), 1.89–1.84 (m, 1H), 1.72–1.66 (m, 1H), 1.34 (s, 3H), 0.89 (s, 9H), 0.05 (s, 3H), 0.05 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 59.84, 55.70, 54.29, 39.90, 26.02, 21.67, 18.34, −5.25, −5.27; HRMS (DART): Calcd for C$_{11}$H$_{24}$O$_2$Si [M+H$^+$]: 217.16183. Found: 217.16185. specific rotation: [α]$_D^{20}$ −12.0 (c = 0.37, CHCl$_3$) for an enantiomerically enriched sample of >99:1 e.r. Enantiomeric purity (>99:1) was determined by chiral GC analysis (using a Supelco β-Dex 225 column) in comparison with authentic racemic material.
**Methyl 2-methyloxirane-2-carboxylate (2s)**

Following general procedure B, 2s was produced as a colorless oil (4.38 g, 40%). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 3.76 (s, 3H), 3.11 (d, 1H, $J = 6.1$ Hz), 2.77 (d, 1H, $J = 6.0$ Hz), 1.58 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 171.31, 53.86, 53.15, 52.77, 17.59; HRMS (DART): Calcd for C$_5$H$_8$O$_3$ [M+H]$^+$: 117.05462. Found: 117.05497.

**Tert-butyl 2-methyloxirane-2-carboxylate (2t)**

Following general procedure B, 2t was produced as a colorless oil (9.77 g, 50%). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 3.04 (d, 1H, $J = 6.1$ Hz), 2.69 (d, 1H, $J = 6.2$ Hz), 1.53 (s, 3H), 1.47 (s, 9H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 169.85, 82.24, 54.36, 53.01, 28.03, 17.67; HRMS (DART): Calcd for C$_8$H$_{14}$O$_3$ [M+H]$^+$: 159.10157. Found: 159.10165.
**β-Lactones**

**4,4-Dimethyloxetan-2-one (3a)**

Following general procedure C, 3a was produced in 78% yield (determined by $^1$H NMR versus hexamethyldisiloxane as an internal standard) as a colorless oil. Analytical data match literature values. $^1$H NMR (500 MHz, CDCl$_3$): δ 3.16 (s, 2H), 1.59 (s, 6H); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 167.48, 76.18, 48.64, 26.37.

**4-Ethyl-4-methyloxetan-2-one (3b)**

Following general procedure C, 3b was produced in 51% yield (determined by $^1$H NMR versus hexamethyldisiloxane as an internal standard) as a colorless oil. $^1$H NMR (500 MHz, CDCl$_3$): δ 3.18 (d, 1H, $J = 16.1$ Hz), 3.10 (d, 1H, $J = 16.1$ Hz), 1.93–1.81 (m, 2H), 1.57 (s, 3H), 1.02 (t, 3H, $J = 7.5$ Hz); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 168.30, 79.22, 47.02, 32.43, 23.96, 8.55; HRMS (DART): Calcd for C$_6$H$_{10}$O$_2$ [M+H]$^+$: 115.07536. Found: 115.07565.

**4-Methyl-4-propyloxetan-2-one (3c)**

Following general procedure C, 3c was produced as a colorless oil (33.4 mg, 66%). $^1$H NMR (500 MHz, CDCl$_3$): δ 3.18 (d, 1H, $J = 16.1$ Hz), 3.10 (d, 1H, $J = 16.1$ Hz), 1.87–1.75 (m, 2H), 1.57 (s, 3H), 1.50–0.98 (m, 2H), 0.98 (t, 3H, $J = 7.4$ Hz); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 168.36, 78.82, 47.62, 41.64, 24.38, 17.77, 14.23; HRMS (DART): Calcd for C$_7$H$_{12}$O$_2$ [M+H]$^+$: 129.09101. Found: 129.09123.

**4-Isopropyl-4-methyloxetan-2-one (3d)**

Following general procedure C, 3d was produced as a colorless oil (20.6 mg, 79%). $^1$H NMR (500 MHz, CDCl$_3$): δ 3.17 (d, 1H, $J = 16.1$ Hz), 3.02 (d, 1H, $J = 16.1$ Hz), 2.05 (sep, 1H, $J = 6.9$ Hz), 1.50 (s, 3H), 1.02 (d, 3H, $J = 6.8$ Hz), 0.97 (d, 3H, $J = 7.0$ Hz); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 168.53, 81.58, 46.55, 36.23, 20.25, 17.30, 16.72; HRMS (DART): Calcd for C$_7$H$_{12}$O$_2$ [M+H]$^+$: 129.09101. Found: 129.09109.
4-(Tert-butyl)-4-methyloxetan-2-one (3e)

Following general procedure C, 3e was produced as a colorless oil (55.7 mg, 70%). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 3.37 (d, 1H, \(J = 16.3\) Hz), 2.92 (d, 1H, \(J = 16.3\) Hz), 1.58 (s, 3H), 1.04 (s, 9H); \(^1^3\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 168.70, 83.19, 44.59, 36.03, 24.63, 21.78; HRMS (DART): Calcd for C\(_8\)H\(_{14}\)O\(_2\) [M+H]\(^+\): 143.10666. Found: 143.10686.

4-Methyl-4-pentyloxetan-2-one (3f)

Following general procedure C, 3f was produced as a colorless oil (51.2 mg, 79%). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 3.18 (d, 1H, \(J = 16.1\) Hz), 3.10 (d, 1H, \(J = 16.1\) Hz), 1.88–1.76 (m, 2H), 1.57 (s, 3H), 1.44–1.29 (m, 6H), 0.92–0.88 (m, 3H); \(^1^3\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 168.38, 78.90, 47.58, 39.51, 31.86, 24.42, 24.06, 22.61, 14.07; HRMS (DART): Calcd for C\(_9\)H\(_{16}\)O\(_2\) [M+H]\(^+\): 157.12231. Found: 157.12246.

4-Hexyl-4-methyloxetan-2-one (3g)

Following general procedure C, 3g was produced as a colorless oil (59.1 mg, 88%). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 3.18 (d, 1H, \(J = 16.1\) Hz), 3.10 (d, 1H, \(J = 16.1\) Hz), 1.88–1.76 (m, 2H), 1.57 (s, 3H), 1.41–1.29 (m, 8H), 0.91–0.88 (m, 3H); \(^1^3\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 168.39, 78.91, 47.58, 39.55, 31.76, 29.37, 24.43, 24.36, 22.66, 14.18; HRMS (DART): Calcd for C\(_{10}\)H\(_{18}\)O\(_2\) [M+H]\(^+\): 171.13796. Found: 171.13813.

4-Methyl-4-nonyloxetan-2-one (3h)

Following general procedure C, 3h was produced as a colorless oil (39.2 mg, 46%). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 3.18 (d, 1H, \(J = 16.1\) Hz), 3.10 (d, 1H, \(J = 16.1\) Hz), 1.88–1.76 (m, 2H), 1.57 (s, 3H), 1.44–1.27 (m, 14H), 0.88 (t, 3H, \(J = 6.8\) Hz); \(^1^3\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 168.39, 78.92, 47.58, 39.56, 32.00, 29.72, 29.60, 29.59, 29.41, 24.43, 24.40, 22.82, 14.26; HRMS (DART): Calcd for C\(_{13}\)H\(_{24}\)O\(_2\) [M+H]\(^+\): 212.18491. Found: 213.18496.
4-(Cyclopentylmethyl)-4-methyloxetan-2-one (3i)

Following general procedure C, 3i was produced as a colorless oil (66.1 mg, 78%). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 3.21 (d, 1H, $J = 16.1$ Hz), 3.11 (d, 1H, $J = 16.1$ Hz), 1.98–1.76 (m, 4H), 1.67–1.63 (m, 2H), 1.60 (s, 3H), 1.56–1.52 (m, 2H), 1.23–1.09 (m, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 168.45, 79.08, 48.27, 45.14, 36.64, 33.59, 33.48, 25.12, 24.89, 24.86; HRMS (DART): Calcd for C$_{10}$H$_{16}$O$_2$ [M+H]$^+$: 169.12231. Found: 169.12241.

4,4-Diethyloxetan-2-one (3j)

Following general procedure C, 3j was produced in 47% yield (determined by $^1$H NMR versus hexamethyldisiloxane as an internal standard) as a colorless oil. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 3.08 (s, 2H), 1.93–1.80 (m, 4H), 0.98 (t, 6H, $J = 7.5$ Hz); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 168.60, 81.64, 44.87, 29.35, 8.05; HRMS (DART): Calcd for C$_7$H$_{13}$O$_2$ [M+H]$^+$: 129.09101. Found: 129.09113.

1-Oxaspiro[3.5]nonan-2-one (3k)

Following general procedure C, 3k was produced as a colorless oil (39.1 mg, 67%). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 3.07 (s, 2H), 1.92–1.88 (m, 2H), 1.82–1.72 (m, 4H), 1.49–1.44 (m, 4H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 168.69, 79.00, 47.46, 36.00, 24.71, 23.43; HRMS (DART): Calcd for C$_8$H$_{12}$O$_2$ [M+H]$^+$: 141.09101. Found: 141.09109.

Tert-butyl 2-oxo-1-oxa-7-azaspiro[3.5]nonane-7-carboxylate (3l)

Following general procedure C, 3l was produced as a white solid (91.0 mg, 91%). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 3.74–3.72 (m, 2H), 3.34 (ddd, 2H, $J = 3.6, 9.5, 13.4$ Hz), 3.17 (s, 2H), 1.96–1.85 (m, 4H), 1.47 (s, 9H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 167.42, 154.64, 80.28, 76.55, 47.47, 40.65, 35.20, 28.53; HRMS (DART): Calcd for C$_{12}$H$_{19}$NO$_4$ [M+H]$^+$: 242.13868. Found: 242.13886.
**4-Benzyl-4-methyloxetan-2-one (3m)**

Following general procedure C, 3m was produced as a colorless oil (22.5 mg, 67%). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.35–7.27 (m, 3H), 7.23 (app. d, 2H, $J = 7.3$ Hz), 3.25 (d, 1H, $J = 16.2$ Hz), 3.14 (d, 1H, $J = 14.3$ Hz), 3.10 (d, 1H, $J = 14.3$ Hz), 3.09 (d, 1H, $J = 16.3$ Hz), 1.58 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 167.60, 135.23, 130.15, 128.76, 127.49, 78.11, 47.03, 45.28, 24.92; HRMS (DART): Calcd for C$_{11}$H$_{12}$O$_2$ [M+H]$^+$: 177.09101. Found: 177.09121.

**($R$)-4-Methyl-4-phenethyloxetan-2-one ($R$-3n)**

Following general procedure C using ($R$)-2n, ($R$)-3n was produced as a colorless oil (for enantioenriched: 27.7 mg, 42%; for rac: 38.3 mg, 51%). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.31 (app. t, 2H, $J = 7.3$ Hz), 7.24–7.19 (m, 3H), 3.17 (d, 1H, $J = 16.2$ Hz), 3.11 (d, 1H, $J = 16.2$ Hz), 2.82–2.69 (m, 2H), 2.22–2.11 (m, 2H), 1.65 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 168.03, 140.58, 128.82, 128.37, 126.52, 78.35, 47.74, 41.32, 30.66, 24.49; HRMS (DART): Calcd for C$_{12}$H$_{14}$O$_2$ [M+H]$^+$: 191.10666. Found: 191.10669. specific rotation: $[\alpha]_D^{20}$ +3.21 (c = 0.53, CHCl$_3$) for an enantiomerically enriched sample of >99:1 e.r. Enantiomeric purity (>99:1) was determined by HPLC analysis in comparison with authentic racemic material. CHIRALPAK® OD column, 90% hexanes, 10% iPrOH, 1.0 mL/min, 254 nm.
4-Methyl-4-(phenoxyethyl)oxetan-2-one (3o)

Following general procedure C, 3o was produced as a colorless oil (61.7 mg, 81%). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.32–7.29 (m, 2H), 7.02–6.99 (m, 1H), 6.94–6.92 (m, 2H), 4.19 (d, 1H, $J = 10.5$ Hz), 4.11 (d, 1H, $J = 10.5$ Hz), 3.64 (d, 1H, $J = 16.0$ Hz), 3.21 (d, 1H, $J = 16.1$ Hz), 1.71 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 167.08, 158.22, 129.77, 121.88, 114.84, 77.41, 71.00, 45.25, 22.15; HRMS (DART): Calcd for C$_{11}$H$_{12}$O$_3$ [M+H]$^+$: 193.08592. Found: 193.08605.

4-(Chloromethyl)-4-methyloxetan-2-one (3p)

Following general procedure C, 3p was produced as a colorless oil (22.7 mg, 84%). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 3.78–3.73 (m, 2H), 3.49 (d, 1H, $J = 16.4$ Hz), 3.22 (d, 1H, $J = 16.4$ Hz), 1.71 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 166.28, 77.41, 48.84, 46.59, 22.73; HRMS (DART): Calcd for C$_5$H$_7$ClO$_2$ [M+H]$^+$: 135.02073. Found: 135.02097.

4-(((Tert-butyldimethylsilyl)oxy)methyl)-4-methyloxetan-2-one (3q)

Following general procedure C, 3q was produced as a colorless oil (45.5 mg, 99%). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 3.81 (d, 1H, $J = 11.7$ Hz), 3.69 (d, 1H, $J = 11.7$ Hz), 3.48 (d, 1H, $J = 15.8$ Hz), 3.00 (d, 1H, $J = 15.8$ Hz), 1.54 (s, 3H), 0.90 (s, 9H), 0.08 (s, 6H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 167.71, 77.85, 66.38, 43.75, 25.83, 25.80, 21.33, 18.32; HRMS (DART): Calcd for C$_{11}$H$_{22}$O$_3$Si [M+H]$^+$: 231.14110. Found: 231.14125.

(R)-4-(2-((Tert-butyldimethylsilyl)oxy)ethyl)-4-methyloxetan-2-one (R-3r)

Following general procedure C using (R)-2r, (R)-3r was produced as a colorless oil (for rac: 89.3 mg, 91%). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 3.84–3.81 (m, 1H), 3.78–3.75 (m, 1H), 3.51 (d, 1H, $J = 16.3$ Hz), 3.10 (d, 1H, $J = 16.3$ Hz), 2.09–2.05 (m, 2H), 1.61 (s, 3H), 0.88 (s, 9H), 0.69 (s, 3H), 0.05 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 168.61, 77.97, 59.08, 48.39, 41.30, 25.97, 24.98, 18.27, $-5.39$, $-5.44$; HRMS (DART): Calcd for C$_{12}$H$_{24}$SiO$_3$ [M+H]$^+$: 245.15675. Found: 245.15676. specific rotation: $[\alpha]_D^{20} = -9.93$ (c = 0.26, CHCl$_3$) for an enantiomerically enriched
sample of >99:1 e.r. Enantiomeric purity (>99:1) was determined by chiral GC analysis (using an Astec CHIRALDEX A-TA column) in comparison with authentic racemic material.
Methyl 2-methyl-4-oxooxetane-2-carboxylate (3s)

Following general procedure C, 3s was produced as a colorless oil (23.9 mg, 83%). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta 3.84\) (s, 3H), 3.75 (d, 1H, \(J = 16.4\) Hz), 3.36 (d, 1H, \(J = 16.4\) Hz), 1.81 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta 170.26, 165.85, 74.04, 53.38, 48.39, 22.08\); HRMS (DART): Calcd for C\(_6\)H\(_8\)O\(_4\)[M+H]\(^+\): 145.04954. Found: 145.04976.

Tert-butyl 2-methyl-4-oxooxetane-2-carboxylate (3t)

Following general procedure C, 3t was produced as a colorless oil (21.6 mg, 58%). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta 3.69\) (d, 1H, \(J = 16.4\) Hz), 3.30 (d, 1H, \(J = 16.3\) Hz), 1.77 (s, 3H), 1.51 (s, 9H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta 168.82, 166.43, 83.77, 74.54, 48.04, 27.94, 22.00\); HRMS (DART): Calcd for C\(_9\)H\(_{16}\)O\(_2\)[M+H]^+: 187.09649. Found: 187.09666.
Ketone-Aldol Products

Methyl 3-hydroxy-3-methyloctanoate (6f)

Following general procedure D, 6f was produced as a colorless oil (56.6 mg, 91%). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 3.71 (s, 3H), 3.41 (s, 1H), 2.52 (d, 1H, $J = 15.6$ Hz), 2.44 (d, 1H, $J = 15.6$ Hz), 1.51–1.48 (m, 2H), 1.37–1.25 (m, 6H), 1.23 (s, 3H), 0.89 (app. t, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 173.68, 71.15, 51.80, 44.80, 32.40, 23.77, 22.74, 14.17; HRMS (DART): Calcd for C$_{10}$H$_{20}$O$_3$ [M+H]$^+$: 189.14852. Found: 189.14847.

Methyl 3-hydroxy-3-methyl-4-phenylbutanoate (6m)

Following general procedure D, 6m was produced as a colorless oil (29.3 mg, 98%). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.31–7.28 (m, 2H), 7.24–7.21 (m, 3H), 3.70 (s, 3H), 2.89–2.82 (m, 2H), 2.49 (d, 1H, $J = 15.8$ Hz), 2.43 (d, 1H, $J = 15.8$ Hz), 1.25 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 173.48, 137.25, 130.67, 128.31, 126.75, 71.36, 51.85, 48.19, 44.19, 27.28; HRMS (DART): Calcd for C$_{12}$H$_{16}$O$_3$ [M+H]$^+$: 209.11722. Found: 209.11717.

(R)-Methyl 3-hydroxy-3-methyl-5-phenylpentanoate (6n)

Following general procedure D using (R)-3n, (R)-6n was produced as a colorless oil (for enantioenriched: 32.5 mg, 100%; for rac: 40.0 mg, 90%). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.28 (app. t, 2H, $J = 7.8$ Hz), 7.20–7.17 (m, 3H), 3.72 (s, 3H), 3.54 (s, 1H), 2.77–2.66 (m, 2H), 2.59 (d, 1H, $J = 15.7$ Hz), 2.51 (d, 1H, $J = 15.7$ Hz), 1.88–1.78 (m, 2H), 1.32 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 173.57, 142.33, 128.57, 128.48, 125.97, 70.93, 51.89, 44.94, 43.98, 30.42, 26.84; HRMS (DART): Calcd for C$_{13}$H$_{18}$O$_3$ [M+H]$^+$: 223.13287. Found: 223.13280. specific rotation: $[\alpha]$$_{D}^{20}$ $–4.95$ (c = 0.47, CHCl$_3$) for an enantiomerically enriched sample of >99:1 e.r. Enantiomeric purity (>99:1) was determined by HPLC analysis in comparison with authentic racemic material. CHIRALPAK® OD column, 98% hexanes, 2% $^1$PrOH, 1.0 mL/min, 254 nm.
<Peak Table>

| Peak# | Ret. Time | Area   | Area%  |
|-------|-----------|--------|--------|
| 1     | 18.510    | 226198 | 50.070 |
| 2     | 20.433    | 225569 | 49.930 |
| Total |           | 451767 | 100.000|

<Peak Table>

| Peak# | Ret. Time | Area   | Area%  |
|-------|-----------|--------|--------|
| 1     | 20.495    | 147327 | 100.000|
| Total |           | 147327 | 100.000|

(S)-6n

(R)-6n
**Methyl 3-hydroxy-3-methyl-4-phenoxybutanoate (6o)**

Following general procedure D, 6o was produced as a colorless oil (33.3 mg, 96%). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.30–7.27 (m, 2H), 6.96 (app. t, 1H, $J = 7.4$ Hz), 6.90 (app. d, 2H, $J = 7.9$ Hz), 3.92 (d, 1H, $J = 8.9$ Hz), 3.87 (d, 1H, $J = 8.9$ Hz), 3.78 (s, 1H), 3.71 (s, 3H), 2.78 (d, 1H, $J = 15.8$ Hz), 2.63 (d, 1H, $J = 15.8$ Hz), 1.39 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 173.05, 158.66, 129.64, 121.30, 114.71, 74.20, 70.76, 51.93, 42.16, 25.02; HRMS (DART): Calcd for C$_{12}$H$_{16}$O$_4$ [M+H]$^+$: 225.11214. Found: 225.11216.

**Methyl 5-((tert-butyldimethylsilyl)oxy)-3-hydroxy-3-methylpentanoate (6r)**

Following general procedure D, 6r was produced as a colorless oil (85.5 mg, 98%). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 4.20 (s, 1H), 3.88 (app. t, 2H), 3.69 (s, 1H), 2.61 (d, 2H, $J = 14.9$ Hz), 2.55 (d, 2H, $J = 14.9$ Hz), 1.89–1.78 (m, 2H), 1.31 (s, 3H), 0.90 (s, 9H), 0.08 (s, 6H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 172.64, 71.43, 51.69, 45.88, 42.01, 27.17, 26.00, 18.25, –5.41; HRMS (DART): Calcd for C$_{13}$H$_{29}$O$_4$Si [M+H]$^+$: 277.18296. Found: 277.18240. specific rotation: $[\alpha]_D$°$^{-20} = –9.03$ (c = 0.52, CHCl$_3$). We synthesized this aldol product from enantiopure lactone, but we were not able to resolve enantiomers of a racemic sample using chiral HPLC of GC to prove that enantiopurity was maintained. Based on the optical activity of 6r and the fact that the ring-opening of (R)-3n proceeds with complete retention of stereochemistry, we propose that this methanolysis also proceeds in >99:1 e.r.

**1-(Tert-butyl) 4-methyl 2-hydroxy-2-methylsuccinate (6t)**

Following general procedure D, 6t was produced as a colorless oil (23.2 mg, 85%). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 3.69 (s, 1H), 3.68 (s, 3H), 2.90 (d, 1H, $J = 16.1$ Hz), 2.65 (d, 1H, $J = 16.1$ Hz), 1.49 (s, 9H), 1.40 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 174.83, 171.25, 82.64, 72.52, 51.83, 44.29, 27.96, 26.63; HRMS (DART): Calcd for C$_{10}$H$_{18}$O$_5$ [M+H]$^+$: 219.12270. Found: 219.12292.

**((R)-Methyl 3-((tert-butyldimethylsilyl)oxy)-3-methyl-5-phenylpentanoate ((R)-6n-TBS)**

The title compound was synthesized using a procedure adapted from the literature. To a solution of 6n in DCM (0.3M) at 0 °C under a nitrogen atmosphere was added 2,6-lutidine (4.0 eq.) and tert-butyldimethylsilyl trifluoromethanesulfonate (3 eq.). The reaction was allowed to stir at 22 °C and was monitored by $^1$H NMR until starting material was entirely consumed (~5 min). The solution was washed with 1.0 M HCl to remove 2,6-lutidine, and the aqueous layer was extracted with DCM (3x). Organic layers were combined, dried with MgSO$_4$, and concentrated. The crude product was loaded with hexanes onto a column with increasing eluent polarity (100% hexanes, 19:1 hexanes:Et$_2$O). 6n-TBS was produced as a colorless oil (for enantioenriched: 29.9 mg, 69%; for rac: 40.8 mg, 72%). Analytical data match literature values. $^{13}$H NMR (500 MHz, CDCl$_3$): $\delta$
7.29–7.26 (m, 2H), 7.20–7.16 (m, 3H), 3.66 (s, 3H), 2.76–2.65 (m, 2H), 2.57 (s, 2H), 1.89 (d, 1H, \( J = 8.7 \) Hz), 1.87 (d, 1H, \( J = 8.7 \) Hz), 1.42 (s, 3H), 0.89 (s, 9H), 0.12 (s, 3H), 0.12 (s, 3H); \(^{13}\text{C} \text{NMR} \ (125 \text{ MHz, } \text{CDCl}_3): \delta 171.55, 142.74, 128.52, 125.83, 74.59, 51.51, 46.84, 45.02, 30.80, 28.13, 25.93, 18.33, -1.84, -1.92; \text{HRMS} \ (\text{DART}): \text{Calcd for } \text{C}_{19}\text{H}_{32}\text{O}_3\text{Si}[\text{M+H}]^+: 337.21935. \text{Found: 337.21958. specific rotation: } [\alpha]_D^{20} \text{–} 6.67 \ (c = 0.51, \text{CHCl}_3). \text{Comparing to literature data of an enantiomerically enriched sample of 95:5 e.r. ([}\alpha]_D^{25} \text{–} 4.28 \ (c = 0.27, \text{CHCl}_3)), \text{the absolute configuration of } 6n\text{-TBS was determined to be the (R)-stereoisomer.}
Isobutylene oxide (2a), $^1$H NMR spectrum (500 MHz, CDCl$_3$)

Isobutylene oxide (2a), $^{13}$C NMR spectrum (125 MHz, CDCl$_3$)

S31
2-Ethyl-2-methyloxirane (2b), $^1$H NMR spectrum (500 MHz, CDCl$_3$)

2-Ethyl-2-methyloxirane (2b), $^{13}$C NMR spectrum (125 MHz, CDCl$_3$)
2-Methyl-2-propyloxirane (2c), $^1$H NMR spectrum (500 MHz, CDCl$_3$)

2-Methyl-2-propyloxirane (2c), $^{13}$C NMR spectrum (125 MHz, CDCl$_3$)
2-Isopropyl-2-methyloxirane (2d), $^1$H NMR spectrum (500 MHz, CDCl$_3$)

2-Isopropyl-2-methyloxirane (2d), $^{13}$C NMR spectrum (125 MHz, CDCl$_3$)

S34
2-(Tert-butyl)-2-methyloxirane (2e), $^1$H NMR spectrum (500 MHz, CDCl$_3$)

2-(Tert-butyl)-2-methyloxirane (2e), $^{13}$C NMR spectrum (125 MHz, CDCl$_3$)
2-Methyl-2-pentyloxirane (2f), $^1$H NMR spectrum (500 MHz, CDCl$_3$)

2-Methyl-2-pentyloxirane (2f), $^{13}$C NMR spectrum (125 MHz, CDCl$_3$)
2-Hexyl-2-methyloxirane (2g), $^1$H NMR spectrum (500 MHz, CDCl$_3$)

2-Hexyl-2-methyloxirane (2g), $^{13}$C NMR spectrum (125 MHz, CDCl$_3$)
2-Methyl-2-nonyloxirane (2h), $^1$H NMR spectrum (500 MHz, CDCl$_3$)

2-Methyl-2-nonyloxirane (2h), $^{13}$C NMR spectrum (125 MHz, CDCl$_3$)
2-(Cyclopentylmethyl)-2-methyloxirane (2i), $^1$H NMR spectrum (500 MHz, CDCl$_3$)

2-(Cyclopentylmethyl)-2-methyloxirane (2i), $^{13}$C NMR spectrum (125 MHz, CDCl$_3$)
2,2-Diethyloxirane (2j), $^1$H NMR spectrum (500 MHz, CDCl$_3$)

2,2-Diethyloxirane (2j), $^{13}$C NMR spectrum (125 MHz, CDCl$_3$)
1-Oxaspiro[2.5]octane (2k), $^1$H NMR spectrum (500 MHz, CDCl$_3$)

1-Oxaspiro[2.5]octane (2k), $^{13}$C NMR spectrum (125 MHz, CDCl$_3$)
2-Benzyl-2-methyloxirane (2m), $^1$H NMR spectrum (500 MHz, CDCl$_3$)

2-Benzyl-2-methyloxirane (2m), $^{13}$C NMR spectrum (125 MHz, CDCl$_3$)
2-Methyl-2-phenyloxirane (2n), $^1$H NMR spectrum (500 MHz, CDCl$_3$)

2-Methyl-2-phenyloxirane (2n), $^{13}$C NMR spectrum (125 MHz, CDCl$_3$)
2-Methyl-2-(phenoxy)methyloxirane (2o), $^1$H NMR spectrum (500 MHz, CDCl$_3$)

2-Methyl-2-(phenoxy)methyloxirane (2o), $^{13}$C NMR spectrum (125 MHz, CDCl$_3$)
**Tert-butyldimethyl((2-methyloxiran-2-yl)methoxy)silane (2q), $^1$H NMR spectrum (500 MHz, CDCl$_3$)**

**Tert-butyldimethyl((2-methyloxiran-2-yl)methoxy)silane (2q), $^{13}$C NMR spectrum (125 MHz, CDCl$_3$)**
**Tert-butyldimethyl(2-(2-methyloxiran-2-yl)ethoxy)silane (2r),** \(^1\text{H NMR spectrum (500 MHz, CDCl}_3\)**

**Tert-butyldimethyl(2-(2-methyloxiran-2-yl)ethoxy)silane (2r),** \(^{13}\text{C NMR spectrum (125 MHz, CDCl}_3\)**
Methyl 2-methyloxirane-2-carboxylate (2s), $^1$H NMR spectrum (500 MHz, CDCl$_3$)

Methyl 2-methyloxirane-2-carboxylate (2s), $^{13}$C NMR spectrum (125 MHz, CDCl$_3$)
*Tert*-butyl 2-methyloxirane-2-carboxylate (2t), $^1$H NMR spectrum (500 MHz, CDCl$_3$)

$^1$H NMR spectrum (500 MHz, CDCl$_3$)

*Tert*-butyl 2-methyloxirane-2-carboxylate (2t), $^{13}$C NMR spectrum (125 MHz, CDCl$_3$)

$^{13}$C NMR spectrum (125 MHz, CDCl$_3$)
4-Ethyl-4-methyloxetan-2-one (3b), $^1$H NMR spectrum (500 MHz, CDCl$_3$)

4-Ethyl-4-methyloxetan-2-one (3b), $^{13}$C NMR spectrum (125 MHz, CDCl$_3$)
4-Methyl-4-propyloxetan-2-one (3c), $^1$H NMR spectrum (500 MHz, CDCl$_3$)

4-Methyl-4-propyloxetan-2-one (3c), $^{13}$C NMR spectrum (125 MHz, CDCl$_3$)
4-Isopropyl-4-methyloxetan-2-one (3d), $^1$H NMR spectrum (500 MHz, CDCl$_3$)

4-Isopropyl-4-methyloxetan-2-one (3d), $^{13}$C NMR spectrum (125 MHz, CDCl$_3$)
4-(Tert-butyl)-4-methyloxetan-2-one (3e), $^1$H NMR spectrum (500 MHz, CDCl$_3$)

4-(Tert-butyl)-4-methyloxetan-2-one (3e), $^{13}$C NMR spectrum (125 MHz, CDCl$_3$)
4-Methyl-4-pentyloxetan-2-one (3f), $^1$H NMR spectrum (500 MHz, CDCl$_3$)

4-Methyl-4-pentyloxetan-2-one (3f), $^{13}$C NMR spectrum (125 MHz, CDCl$_3$)
4-Hexyl-4-methyloxetan-2-one (3g), $^1$H NMR spectrum (500 MHz, CDCl$_3$)

4-Hexyl-4-methyloxetan-2-one (3g), $^{13}$C NMR spectrum (125 MHz, CDCl$_3$)
4-Methyl-4-nonyloxetan-2-one (3h), $^1$H NMR spectrum (500 MHz, CDCl$_3$)

4-Methyl-4-nonyloxetan-2-one (3h), $^{13}$C NMR spectrum (125 MHz, CDCl$_3$)
4-(Cyclopentylmethyl)-4-methyloxetan-2-one (3i), $^1$H NMR spectrum (500 MHz, CDCl$_3$)

4-(Cyclopentylmethyl)-4-methyloxetan-2-one (3i), $^{13}$C NMR spectrum (125 MHz, CDCl$_3$)
4,4-Diethyloxetan-2-one (3j), $^1$H NMR spectrum (500 MHz, CDCl$_3$)

4,4-Diethyloxetan-2-one (3j), $^{13}$C NMR spectrum (125 MHz, CDCl$_3$)
1-Oxaspiro[3.5]nonan-2-one (3k), $^1$H NMR spectrum (500 MHz, CDCl$_3$)

$^1$C NMR spectrum (125 MHz, CDCl$_3$)
**Tert-butyl 2-oxo-1-oxa-7-azaspiro[3.5]nonane-7-carboxylate (3l), $^1$H NMR spectrum (500 MHz, CDCl$_3$)**

![H NMR spectrum](image)

**Tert-butyl 2-oxo-1-oxa-7-azaspiro[3.5]nonane-7-carboxylate (3l), $^{13}$C NMR spectrum (125 MHz, CDCl$_3$)**

![C NMR spectrum](image)
4-Benzyl-4-methyloxetan-2-one (3m), $^1$H NMR spectrum (500 MHz, CDCl$_3$)

4-Benzyl-4-methyloxetan-2-one (3m), $^{13}$C NMR spectrum (125 MHz, CDCl$_3$)
4-Methyl-4-phenyloxetan-2-one (3n), $^1$H NMR spectrum (500 MHz, CDCl$_3$)

4-Methyl-4-phenyloxetan-2-one (3n), $^{13}$C NMR spectrum (125 MHz, CDCl$_3$)
4-Methyl-4-(phenoxy methyl)oxetan-2-one (3o), $^1$H NMR spectrum (500 MHz, CDCl$_3$)

4-Methyl-4-(phenoxy methyl)oxetan-2-one (3o), $^{13}$C NMR spectrum (125 MHz, CDCl$_3$)
4-(Chloromethyl)-4-methyloxetan-2-one (3p), $^1$H NMR spectrum (500 MHz, CDCl$_3$)

4-(Chloromethyl)-4-methyloxetan-2-one (3p), $^{13}$C NMR spectrum (125 MHz, CDCl$_3$)
4-(((Tert-butyldimethylsilyl)oxy)methyl)-4-methyloxetan-2-one (3q), $^1$H NMR spectrum (500 MHz, CDCl$_3$)

4-(((Tert-butyldimethylsilyl)oxy)methyl)-4-methyloxetan-2-one (3q), $^{13}$C NMR spectrum (125 MHz, CDCl$_3$)
4-(2-((Tert-butyldimethylsilyl)oxy)ethyl)-4-methyloxetan-2-one (3r), $^1$H NMR spectrum (500 MHz, CDCl$_3$)

4-(2-((Tert-butyldimethylsilyl)oxy)ethyl)-4-methyloxetan-2-one (3r), $^{13}$C NMR spectrum (125 MHz, CDCl$_3$)
Methyl 2-methyl-4-oxooxetane-2-carboxylate (3s), \(^1\)H NMR spectrum (500 MHz, CDCl\(_3\))

\[
\begin{array}{c}
\text{Me} \quad \text{O} \\
\text{MeO} \\
3s
\end{array}
\]

Methyl 2-methyl-4-oxooxetane-2-carboxylate (3s), \(^{13}\)C NMR spectrum (125 MHz, CDCl\(_3\))

\[
\begin{array}{c}
\text{Me} \quad \text{O} \\
\text{MeO} \\
3s
\end{array}
\]
Tert-butyl 2-methyl-4-oxooxetane-2-carboxylate (3t), $^1$H NMR spectrum (500 MHz, CDCl$_3$)

\[ \text{Me} \quad \text{3t} \]

$^1$C NMR spectrum (125 MHz, CDCl$_3$)

\[ \text{Me} \quad \text{3t} \]
Methyl 3-hydroxy-3-methyloctanoate (6f), $^1$H NMR spectrum (500 MHz, CDCl₃)

Methyl 3-hydroxy-3-methyloctanoate (6f), $^{13}$C NMR spectrum (125 MHz, CDCl₃)
Methyl 3-hydroxy-3-methyl-4-phenylbutanoate (6m), $^1$H NMR spectrum (500 MHz, CDCl$_3$)

Methyl 3-hydroxy-3-methyl-4-phenylbutanoate (6m), $^{13}$C NMR spectrum (125 MHz, CDCl$_3$)
Methyl 3-hydroxy-3-methyl-5-phenylpentanoate (6n), $^1$H NMR spectrum (500 MHz, CDCl$_3$)

Methyl 3-hydroxy-3-methyl-5-phenylpentanoate (6n), $^{13}$C NMR spectrum (125 MHz, CDCl$_3$)
Methyl 3-hydroxy-3-methyl-4-phenoxybutanoate (6o), $^1$H NMR spectrum (500 MHz, CDCl$_3$)

Methyl 3-hydroxy-3-methyl-4-phenoxybutanoate (6o), $^{13}$C NMR spectrum (125 MHz, CDCl$_3$)
Methyl 5-((tert-butyldimethylsilyl)oxy)-3-hydroxy-3-methylpentanoate (6r), $^1$H NMR spectrum (500 MHz, CDCl$_3$)

Methyl 5-((tert-butyldimethylsilyl)oxy)-3-hydroxy-3-methylpentanoate (6r), $^{13}$C NMR spectrum (125 MHz, CDCl$_3$)
1-(Tert-butyl) 4-methyl 2-hydroxy-2-methylsuccinate (6t), $^1$H NMR spectrum (500 MHz, CDCl$_3$)

1-(Tert-butyl) 4-methyl 2-hydroxy-2-methylsuccinate (6t), $^{13}$C NMR spectrum (125 MHz, CDCl$_3$)
methyl 3-((tert-butyldimethylsilyl)oxy)-3-methyl-5-phenylpentanoate (6n-TBS), $^1$H NMR spectrum (500 MHz, CDCl$_3$)

methyl 3-((tert-butyldimethylsilyl)oxy)-3-methyl-5-phenylpentanoate (6n-TBS), $^{13}$C NMR spectrum (125 MHz, CDCl$_3$)
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