# Supporting Information

**Carbonylative enantioselective meso-desymmetrization of cis-epoxides to trans-β-lactones: effect of electronic variation on enantioselectivity**

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## Synthesis of starting materials

| (Z)-1,8-Bis(2,2,2-trifluoroethoxy)oct-4-ene (SM1) | S13 |
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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. High-pressure reactions were performed in a custom-designed and -fabricated, six-chamber, stainless steel, high-pressure reactor. The reactor design allowed for incorporation of six 1 or 2 fluid dram glass vials. 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 (unless indicated otherwise) with shifts reported relative to the residual solvent peak (CDCl$_3$: 7.26 ppm ($^1$H), and 77.16 ppm ($^{13}$C); C$_6$D$_6$: 7.16 ppm ($^1$H) and 128.06 ppm ($^{13}$C)). $^{19}$F NMR spectra were recorded on a Varian 400 or 500 MHz instrument at 22 °C (unless indicated otherwise) with shifts referenced to an external standard of neat CFCl$_3$ (0 ppm) or neat C$_6$F$_6$ (164.9 ppm); both external standards were recorded at 22 °C. All J values are given in Hertz. NMR solvents were purchased from Cambridge Isotope Laboratories and stored over activated 4Å molecular sieves (C$_6$D$_6$) or K$_2$CO$_3$ (CDCl$_3$). Optical rotations were measured on a Perkin-Elmer 241 polarimeter, and are given in 10$^{-1}$ deg cm$^2$ g$^{-1}$. GC analyses were performed on a Hewlett Packard 6890 gas chromatograph equipped with a Supelco β-Dex120 and a Supelco β-Dex225 column, and a flame ionization detector. Helium (Airgas, UHP grade) was used as carrier gas. Reported percentages of epoxide, ketone, and β-lactone are uncorrected relative areas. HRMS analyses were either performed at the Mass Spectrometry Laboratory at the University of Illinois at Urbana-Champaign (ESI) or on a Thermo Scientific Exactive Orbitrap MS system with an Ion Sense DART ion source (Cornell University).

Chemicals

Anhydrous 1,4-dioxane, 1,2-dimethoxyethane (DME) and tetrahydropyran (THP) were purchased from Sigma-Aldrich and degassed via three freeze-pump-thaw cycles prior to use. Anhydrous toluene, dichloromethane (DCM), hexanes, 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 and dichloromethane were degassed via three freeze-pump-thaw cycles prior to use.

Triethylamine was 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.

Carbon monoxide (Airgas, 99.99% min. purity) was used as received. All other chemicals were purchased from Aldrich, Alfa-Aesar, Combi-Blocks, or GFS Chemicals 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.

The following compounds were prepared according to literature procedures:

a) catalysts and catalyst precursors

NaCo(CO)$_4$,\(^2\)

\[(S,S)\text{-salcyAl(THF)}_2]^-\ [\text{Co(CO)}_4]^+ \ (S,S)\text{-salcy} = (S,S)\text{-}N,N'\text{-bis}(3,5\text{-di-}\text{ tert-butyl-salicylidene})\text{-}1,2\text{-cyclohexanediameine}\),\(^3\)

(R)$^1$BuBinamAlCl (precursor to (R)-1a, (R)$^1$BuBinam $=$ (R)$N,N'$-bis(2-hydroxy-3,5-di-\text{ tert-butylbenzylidene})\text{-}1,1'$\text{-binaphthyl}-2,2'$\text{-diamine}$),\(^4\)

(R)-Xyl$_2$BinamAlCl (precursor to (R)-1b, (R)-Xyl$_2$Binam $=$ (R)$5',5''\text{-}((1E,1'E)-(\text{[1,1'\text{-binaphthalene}]2,2'}\text{-diiylbis(azanylylidene)})\text{bis(methanylylidene)})\text{bis}(2,2'',6,6''\text{-tetramethyl-}[1,1':3',1''\text{-terphenyl}]\text{-}4'\text{-olate})$,\(^5\)

(R)-pMeMesBinamAlCl (precursor to (R)-1c, (R)-pMeMesBinam $=$ (R)$3,3''\text{-}((\text{[1,1'\text{-binaphthalene}]2,2'}\text{-diiylbis(azanylylidene)})\text{bis(methanylylidene)})\text{bis}(2',4',5,6'\text{-tetramethyl-}[1,1'\text{-biphenyl}]\text{-}2\text{-olate})$,\(^5\)
b) epoxides

meso-(2R,3S)-2,3-dipropyloxirane (3a),
meso-(2R,3S)-2,3-diethyloxirane (3c),
meso-(2R,3S)-2,3-dibutyloxirane (3d),

c) others

(Z)-oct-4-ene-1,8-diylbis(4-methylbenzenesulfonate)
Table S1. Expanded Table 1 – Evaluation of enantiopure [Lewis acid]\[Co(CO)₄\]^− catalysts and reaction parameters for the carbonylative enantioselective desymmetrization of meso-epoxide 3a

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalysta</th>
<th>Solvent</th>
<th>Conv. (%)</th>
<th>% ee</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>(R)-1c</td>
<td>THF</td>
<td>70</td>
<td>94</td>
</tr>
<tr>
<td>2</td>
<td>(S,S)-2</td>
<td>THF</td>
<td>43</td>
<td>16</td>
</tr>
<tr>
<td>3</td>
<td>(R)-1a</td>
<td>THF</td>
<td>89</td>
<td>58</td>
</tr>
<tr>
<td>4</td>
<td>(R)-1b</td>
<td>THF</td>
<td>42</td>
<td>97</td>
</tr>
<tr>
<td>5</td>
<td>(R)-1c</td>
<td>THP</td>
<td>78</td>
<td>73</td>
</tr>
<tr>
<td>6</td>
<td>(R)-1c</td>
<td>1,4-dioxane</td>
<td>98</td>
<td>70</td>
</tr>
<tr>
<td>7</td>
<td>(R)-1c</td>
<td>DME</td>
<td>7</td>
<td>24</td>
</tr>
<tr>
<td>8</td>
<td>(R)-1c</td>
<td>toluene</td>
<td>98</td>
<td>43</td>
</tr>
<tr>
<td>9c</td>
<td>(R)-1c</td>
<td>THF</td>
<td>65</td>
<td>94</td>
</tr>
<tr>
<td>10d</td>
<td>(R)-1c</td>
<td>THF</td>
<td>&gt;95</td>
<td>87</td>
</tr>
</tbody>
</table>

aCatalysts were generated in situ (L₉AlCl + NaCo(CO)₄), except for catalyst (S,S)-2.
bConversion to β-lactone 4a and enantiomeric excess determined by GC analysis.
c5 mol % Na[Co(CO)₄] added.
dRun at 40 °C.
Table S2. Expanded Table 2 – Scope of the carbonylative enantioselective desymmetrization of meso-epoxides 3 using catalysts (R)-1b and 1c

<table>
<thead>
<tr>
<th>Entry</th>
<th>R</th>
<th>Catalyst</th>
<th>mol % Catalyst</th>
<th>% Isol. Yield 4</th>
<th>er c of 4</th>
<th>% Ketone side product c</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Me</td>
<td>(4b)</td>
<td>(R)-1c</td>
<td>2.5</td>
<td>95d</td>
<td>91.5 : 8.5</td>
</tr>
<tr>
<td>2</td>
<td>Et</td>
<td>(4c)</td>
<td>(R)-1c</td>
<td>4</td>
<td>70</td>
<td>97.8 : 2.2</td>
</tr>
<tr>
<td>3</td>
<td>nPr</td>
<td>(4a)</td>
<td>(R)-1c</td>
<td>7</td>
<td>77</td>
<td>96.9 : 3.1</td>
</tr>
<tr>
<td>4</td>
<td>nBu</td>
<td>(4d)</td>
<td>(R)-1c</td>
<td>8</td>
<td>72</td>
<td>95.9 : 4.1</td>
</tr>
<tr>
<td>5e</td>
<td>(CH₂)₃OCH₂CF₃ (4e)</td>
<td>(R)-1c</td>
<td>12.5</td>
<td>79</td>
<td>92.0 : 8.0</td>
<td>n.d. f</td>
</tr>
<tr>
<td>6</td>
<td>Me</td>
<td>(4b)</td>
<td>(R)-1b</td>
<td>2.5</td>
<td>94d</td>
<td>91.3 : 8.7</td>
</tr>
<tr>
<td>7</td>
<td>Et</td>
<td>(4c)</td>
<td>(R)-1b</td>
<td>6</td>
<td>74</td>
<td>99.0 : 1.0</td>
</tr>
<tr>
<td>8</td>
<td>nPr</td>
<td>(4a)</td>
<td>(R)-1b</td>
<td>10</td>
<td>76</td>
<td>98.6 : 1.4</td>
</tr>
<tr>
<td>9</td>
<td>nBu</td>
<td>(4d)</td>
<td>(R)-1b</td>
<td>12</td>
<td>72</td>
<td>95.6 : 4.4</td>
</tr>
</tbody>
</table>

aAll reactions gave full conversion by GC analysis. bCatalysts (R)-1b and 1c were generated in situ (L₃AlCl + NaCo(CO)₄). cDetermined by GC analysis. dYield determined by GC analysis using method of standard addition. eRun at 33 °C. fNot determined.

Note: Substrate 3e (meso-2,3-bis(3-(2,2,2-trifluoroethoxy)propyl)oxirane, p. S13) is not included in Table 2 in the manuscript. We were unable to obtain the expected 1 : 1 area ratio for the two enantiomers of the corresponding racemic β-lactone 4e on our GC columns (p. S44). As a result, the enantiomeric ratio given for 4e in Table S2 and on p. S44 should be viewed as an approximate value.
Table S3. Expanded Table 3 – Electronic series data including control reactions at low conversion$^a$

<table>
<thead>
<tr>
<th>Entry</th>
<th>R</th>
<th>Catalyst</th>
<th>Ratio at end of reaction (%)</th>
<th>er of 4</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>β-Lactone</td>
<td>Ketone</td>
<td>Epoxide</td>
</tr>
<tr>
<td>1$^{a,d}$</td>
<td>Me (4b)</td>
<td>(R)-1d</td>
<td>94</td>
<td>6</td>
</tr>
<tr>
<td>2$^{a,d}$</td>
<td>Me (4b)</td>
<td>(R)-1c</td>
<td>97</td>
<td>3</td>
</tr>
<tr>
<td>3$^{a,d}$</td>
<td>Me (4b)</td>
<td>(R)-1e</td>
<td>84</td>
<td>4</td>
</tr>
<tr>
<td>4$^{a,d}$</td>
<td>Me (4b)</td>
<td>(R)-1f</td>
<td>97</td>
<td>3</td>
</tr>
<tr>
<td>5</td>
<td>Et (4c)</td>
<td>(R)-1d</td>
<td>87</td>
<td>5</td>
</tr>
<tr>
<td>6$^c$</td>
<td>Et (4c)</td>
<td>(R)-1c</td>
<td>96</td>
<td>4</td>
</tr>
<tr>
<td>7$^c$</td>
<td>Et (4c)</td>
<td>(R)-1e</td>
<td>96</td>
<td>4</td>
</tr>
<tr>
<td>8</td>
<td>Et (4c)</td>
<td>(R)-1f</td>
<td>96</td>
<td>4</td>
</tr>
<tr>
<td>9 $^a$</td>
<td>nPr (4a)</td>
<td>(R)-1d</td>
<td>58</td>
<td>5</td>
</tr>
<tr>
<td>10</td>
<td>nPr (4a)</td>
<td>(R)-1c</td>
<td>81</td>
<td>6</td>
</tr>
<tr>
<td>11</td>
<td>nPr (4a)</td>
<td>(R)-1e</td>
<td>94</td>
<td>3</td>
</tr>
<tr>
<td>12</td>
<td>nPr (4a)</td>
<td>(R)-1f</td>
<td>95</td>
<td>2</td>
</tr>
<tr>
<td>13</td>
<td>nBu (4d)</td>
<td>(R)-1d</td>
<td>64</td>
<td>9</td>
</tr>
<tr>
<td>14</td>
<td>nBu (4d)</td>
<td>(R)-1c</td>
<td>83</td>
<td>11</td>
</tr>
<tr>
<td>15</td>
<td>nBu (4d)</td>
<td>(R)-1e</td>
<td>92</td>
<td>4</td>
</tr>
<tr>
<td>16$^c$</td>
<td>nBu (4d)</td>
<td>(R)-1f</td>
<td>84</td>
<td>3</td>
</tr>
<tr>
<td>17$^c$</td>
<td>nBu (4d)</td>
<td>(R)-1f</td>
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<td>1</td>
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<tr>
<td>18$^f$</td>
<td>Me (4b)</td>
<td>(R)-1f</td>
<td>93$^c$</td>
<td>7$^c$</td>
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<td>$^{nBu}$ (4d)</td>
<td>(R)-1f</td>
<td>38</td>
<td>3</td>
<td>59</td>
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</table>

$^a$Reaction conditions: [3] = 0.5 M, 22 °C, 20 h. Conversion at end of reaction and enantiomeric ratio (er) determined by GC analysis. $^b$% Values were rounded to the nearest percent. $^c$4 mol % catalyst. $^d$Conversion at end of reaction determined by $^1$H NMR spectroscopy. $^e$2.5 h. $^f$Both epoxides combined in one pot ([Epox]$_{\text{total}}$ = 0.5 M) for 6 h. Catalysts (R)-1c–1f were generated in situ (L$_n$AlCl + NaCo(CO)$_4$).
Table S4. Expanded Table 4 – Carbonylation with the best catalyst for each substrate at different temperatures\textsuperscript{a}

<table>
<thead>
<tr>
<th>Entry</th>
<th>R</th>
<th>Catalyst</th>
<th>Temp (°C)</th>
<th>Ratio at end of reaction (%)\textsuperscript{b}</th>
<th>er</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Me (4b)</td>
<td>(R)-1d</td>
<td>0</td>
<td>50 &lt;1 50</td>
<td>93.7 : 6.3</td>
</tr>
<tr>
<td>2</td>
<td>Et (4c)</td>
<td>(R)-1f</td>
<td>0</td>
<td>54 2 44</td>
<td>98.9 : 1.1</td>
</tr>
<tr>
<td>3</td>
<td>Me (4b)</td>
<td>(R)-1d</td>
<td>0</td>
<td>96 4 &lt;1</td>
<td>93.9 : 6.1</td>
</tr>
<tr>
<td>4</td>
<td>Me (4b)</td>
<td>(R)-1d</td>
<td>22</td>
<td>94 6 &lt;1</td>
<td>93.0 : 7.0</td>
</tr>
<tr>
<td>5</td>
<td>Et (4c)</td>
<td>(R)-1f</td>
<td>0</td>
<td>85 2 13</td>
<td>98.8 : 1.2</td>
</tr>
<tr>
<td>6</td>
<td>Et (4c)</td>
<td>(R)-1f</td>
<td>22</td>
<td>96 4 &lt;1</td>
<td>98.4 : 1.6</td>
</tr>
<tr>
<td>7</td>
<td>\textsuperscript{\textsuperscript{b}}Pr (4a)</td>
<td>(R)-1f</td>
<td>0</td>
<td>32 2 66</td>
<td>98.3 : 1.7</td>
</tr>
<tr>
<td>8</td>
<td>\textsuperscript{\textsuperscript{b}}Pr (4a)</td>
<td>(R)-1f</td>
<td>22</td>
<td>95 2 4</td>
<td>97.9 : 2.1</td>
</tr>
<tr>
<td>9</td>
<td>\textsuperscript{\textsuperscript{b}}Bu (4d)</td>
<td>(R)-1f</td>
<td>0</td>
<td>58 2 40</td>
<td>98.5 : 1.5</td>
</tr>
<tr>
<td>10</td>
<td>\textsuperscript{\textsuperscript{b}}Bu (4d)</td>
<td>(R)-1f</td>
<td>22</td>
<td>84 3 14</td>
<td>97.9 : 2.1</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Reaction conditions: [3] = 0.5 M (22 °C) or 1.5 M (0 °C), 21 h, 5 mol % catalyst. Conversion and enantiomeric ratio determined by GC analysis. \textsuperscript{b}Values were rounded to the nearest percent. \textsuperscript{c}Conversion determined by \textsuperscript{1}H NMR of the crude reaction mixture. \textsuperscript{d}5 h. \textsuperscript{e}3 mol % catalyst. \textsuperscript{f}4 mol % catalyst. Catalysts (R)-1d and 1f were generated \textit{in situ} (L\textsubscript{n}AlCl + NaCo(CO)\textsubscript{4}).
Synthetic procedures

**General procedure A: Epoxidation of alkenes to epoxides using mCPBA**

mCPBA (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 the same temperature until TLC analysis indicated complete consumption of the alkene. After destroying excess mCPBA by adding aqueous NaHSO\(_3\) at 0 °C, the reaction mixture was filtered, the organic phase washed with NaHCO\(_3\) (sat., aq., 3x), dried with sodium sulfate, filtered and concentrated under reduced pressure. The residue was purified *via* flash column chromatography.

**General procedure B: Kumada coupling of 2-bromophenols with mesitylmagnesium 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 mesitylmagnesium bromide (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.

**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 or recrystallization.

**General procedure D: Imine condensation of salicylaldehydes onto (R)-2,2′-diamine-1,1′-binaphthalene ([(R)-DABN])**

The corresponding salicylaldehyde, (R)-2,2′-diamine-1,1′-binaphthalene, and methanol 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 then dried *in vacuo* at 80 °C.

**General procedure E: Metalation of salen-compounds using Et$_2$AlCl**

Et$_2$AlCl (Aldrich, 0.98 M, hexanes, *pyrophoric*) was added to a solution of the corresponding salen-compound in DCM (0.04 M) at 0 °C. The resulting solution was stirred at 22 °C for 12 h. Volatiles were removed *in vacuo*, the solid was washed with hexanes, cannula filtered, and dried *in vacuo* overnight.

**General procedure F: Carbonylation of epoxides using (R)-1b–1f**

In a glove box, a 1 or 2 fluid dram glass vial equipped with a Teflon-coated magnetic stir bar was charged with the appropriate precursor to (R)-1b–1f, NaCo(CO)$_4$, and THF. After 1 minute of stirring at 22 °C, the vial was placed in a custom-made 6-well high-pressure reactor which itself was placed in a glove box freezer (−32 °C) for 30 minutes. The appropriate epoxide (also cooled to −32 °C) was then added to the vial, the reactor removed from the freezer, subsequently sealed, taken out of the glove box, placed in a well-ventilated hood and pressurized with carbon monoxide (900 psi). It is important to keep the temperature of the reactor below 0 °C once it is removed from the freezer to minimize isomerization of the epoxide to ketone products. The reactor was then sealed again, placed in a 22 °C water bath (unless noted otherwise) and the reaction mixture stirred for the time indicated. The reactor was then carefully vented in a well-ventilated hood and the product isolated as indicated.
General procedure G: Carbonylation of epoxides using (R)-1d or (R)-1f at 0 °C

In a glove box, a 1 fluid dram glass vial equipped with a Teflon-coated magnetic stir bar was charged with the appropriate precursor to (R)-1d or 1f, NaCo(CO)$_4$, and THF. After 1 minute of stirring at 22 °C, the vial was placed in a custom-made 6-well high-pressure reactor which itself was placed in a glove box freezer (−32 °C) for 30 minutes. The appropriate epoxide (also cooled to −32 °C) was then added to the vial, the reactor removed from the freezer, subsequently sealed, taken out of the glove box, placed in a well-ventilated hood and pressurized with carbon monoxide (900 psi). It is important to keep the temperature of the reactor below 0 °C once it is removed from the freezer to minimize isomerization of the epoxide to ketone products. The reactor was then sealed again, placed in a 0 °C ice bath in an insulated box and the reaction mixture stirred for 21 hours (unless otherwise noted). The reactor was then carefully vented in a well-ventilated hood and the crude reaction mixture run through a silica plug to remove the catalyst. The product was then analyzed by $^1$H NMR spectroscopy and chiral gas chromatography.
Synthesis of starting materials

(Z)-1,8-Bis(2,2,2-trifluoroethoxy)oct-4-ene (SM1)

2,2,2-Trifluoroethanol (1.51 g, 15.1 mmol) was added dropwise to a mixture of sodium hydride (Aldrich, 95 %, dry, 0.480 g, 20.0 mmol) and THF (10 ml) at 0 °C. After stirring for 1 h at 22 °C, a solution of (Z)-oct-4-ene-1,8-diylbis(4-methylbenzene-sulfonate) in THF (5 ml) was added at 0 °C, and the resulting mixture refluxed for 12 h. The reaction mixture was then cooled to 22 °C, H₂O was added, followed by extraction of the aqueous phase with Et₂O (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 to afford SM1 (1.38 g, 85 %) as a colorless liquid. ¹H NMR (400 MHz, CDCl₃): δ 5.38 (ddd, J = 5.7, 4.4, 1.1, 2H), 3.79 (q, J = 8.8, 4H), 3.59 (t, J = 6.4, 4H), 2.12 (td, J = 7.2, 5.4, 4H), 1.67 (dt, J = 7.8, 6.5, 4H). ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 129.7, 124.3 (d, J = 281.4), 72.2, 68.4 (q, J = 33.8), 29.5, 23.4. ¹⁹F NMR (376 MHz, CDCl₃, ref. CFCl₃): δ −74.4 (t, J = 8.8). IR (neat, cm⁻¹): 2935, 1441, 1275, 1133, 966, 827. HRMS (ESI) m/z calculated for C₁₂H₁₈F₆NaO₂⁺ (M + Na⁺) 331.1103, found 331.1110.

2,3-Bis(3-(2,2,2-trifluoroethoxy)propyl)oxirane (3e)

Following general procedure A, (Z)-1,8-bis(2,2,2-trifluoroethoxy)oct-4-ene (SM1, 1.28 g, 4.15 mmol) was reacted with mCPBA (1.41 g) in DCM (10 ml) to give 3e (1.19 g, 88 %) as a colorless liquid. ¹H NMR (400 MHz, C₆D₆): δ 3.23 (q, J = 8.8, 4H), 3.16–3.05 (m, 4H), 2.62–2.57 (m, 2H), 1.52–1.28 (m, 8H). ¹³C{¹H} NMR (101 MHz, C₆D₆): δ 124.7 (d, J = 279.6), 72.0, 68.1 (q, J = 33.4), 56.2, 27.0, 24.6. ¹⁹F NMR (376 MHz, C₆D₆, ref.
CFCl₃: δ ~74.2 (t, J = 8.9). IR (neat, cm⁻¹): 2935, 1444, 1275, 1131, 966, 826. HRMS (ESI) m/z calculated for C₁₂H₁₉F₆O₃⁺ (M + H⁺) 325.1233, found 325.1245.

5-Methoxy-2’,4’,6’-trimethyl-[1,1’-biphenyl]-2-ol (SM2)

Following general procedure B, 2-bromo-4-methoxyphenol (2.86 g, 14.1 mmol) was treated with sodium hydride (0.506 g, 20.0 mmol) in THF (28 ml), followed by addition of Pd(OAc)₂ (0.160 g, 0.696 mmol, 4.93 mol %), and mesitylmagnesium bromide (1 M, THF, 27 ml, 27.0 mmol) to give SM2 (3.30 g, 65 %) as a yellow oil. Analytical data for SM2 has previously been reported.¹⁰ ¹H NMR (400 MHz, CDCl₃): δ 6.99 (s, 2H), 6.92 (d, J = 8.8, 1H), 6.84 (dd, J = 8.8, 3.0, 1H), 6.58 (d, J = 3.0, 1H), 4.29 (s, 1H), 3.76 (s, 3H), 2.34 (s, 3H), 2.04 (s, 6H). ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 153.5, 146.6, 137.9, 137.5, 132.2, 128.6, 127.1, 115.9, 115.0, 114.2, 55.6, 21.0, 20.2.

2-Hydroxy-5-methoxy-2’,4’,6’-trimethyl-[1,1’-biphenyl]-3-carbaldehyde (SM3)

Following general procedure C, 5-methoxy-2’,4’,6’-trimethyl-[1,1’-biphenyl]-2-ol (SM2, 2.66 g, 11.0 mmol) was treated with methylmagnesium bromide (4.1 ml, 12.3 mmol) in THF (20 ml), followed by addition of toluene (38 ml), triethylamine (2.5 ml, 34.0 mmol), and paraformaldehyde (0.824 g, 27.5 mmol). The product was recrystallized from methanol to give SM3 (2.90 g, 98 %) as a gold-colored powder. MP 59–61 °C. ¹H NMR (400 MHz, CDCl₃): δ 10.73 (s, 1H), 9.93 (s, 1H), 7.04 (d, J = 3.1, 1H), 6.99 (d, J = 3.1, 1H), 6.97 (s, 2H), 3.84 (s, 3H), 2.33 (s, 3H), 2.03 (s, 6H). ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 196.3, 153.4, 152.6, 137.6, 136.5, 132.6, 131.2, 128.3, 126.3, 120.3, 114.5, 55.9, 21.2, 20.3. IR (neat, cm⁻¹): 2916, 1652, 1600, 1433, 1316, 1214, 1046, 850, 794,
5-Fluoro-2’,4’,6’-trimethyl-[1,1’-biphenyl]-2-ol (SM4)

Following general procedure B, 2-bromo-4-fluorophenol (2.30 g, 12.0 mmol) was treated with sodium hydride (0.432 g, 17.1 mmol) in THF (24 ml), followed by addition of Pd(OAc)$_2$ (0.136 g, 0.593 mmol, 4.93 mol %), and mesitylmagnesium bromide (1 M, THF, 20 ml, 20.0 mmol) to give SM4 (0.976 g, 35 %) as a yellow oil. $^1$H NMR (400 MHz, CDCl$_3$): δ 6.99 (s, 2H), 6.94 (m, 2H), 6.74 (dd, $J = 8.7, 2.9$, 1H), 4.45 (s, 1H), 2.34 (s, 3H), 2.02 (s, 6H). $^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$): δ 157.1 (d, $J = 238.5$), 148.7 (d, $J = 2.1$), 138.6, 137.7, 131.0, 128.9, 127.6 (d, $J = 7.8$), 116.3 (d, $J = 22.6$), 116.1 (d, $J = 8.4$), 115.4 (d, $J = 23.0$), 21.17, 20.20. $^{19}$F NMR (376 MHz, CDCl$_3$, ref. C$_6$F$_6$): δ −122.7 (td, $J = 8.4, 5.0$). IR (neat, cm$^{-1}$): 3489, 2917, 1611, 1477, 1257, 1178, 1150, 783. HRMS (DART) $m/z$ calculated for C$_{15}$H$_{15}$FO (M$^+$) 230.11014, found 230.11056.

2-Hydroxy-5-fluoro-2’,4’,6’-trimethyl-[1,1’-biphenyl]-3-carbaldehyde (SM5)

Following general procedure C, 5-fluoro-2’,4’,6’-trimethyl-[1,1’-biphenyl]-2-ol (SM4, 2.66 g, 11.6 mmol) was treated with methylmagnesium bromide (4.1 ml, 12.3 mmol) in THF (20 ml), followed by addition of toluene (38 ml), triethylamine (2.5 ml, 34.0 mmol), and paraformaldehyde (0.824 g, 27.5 mmol). The product was recrystallized from methanol to give SM5 (0.958 g, 43 %) as white spindly crystals. MP 119–120 °C. $^1$H NMR (400 MHz, CDCl$_3$): δ 10.89 (s, 1H), 9.92 (s, 1H), 7.28 (dd, $J = 7.5, 3.1$, 1H), 7.12 (dd, $J = 8.5, 3.1$, 1H), 6.97 (s, 2H), 2.33 (s, 3H), 2.02 (s, 6H). $^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$): δ 195.7 (d, $J = 2.5$), 155.5 (d, $J = 241.3$), 155.3 (d, $J = 1.5$), 138.0, 136.4, 132.1
(d, J = 6.7), 131.8 (d, J = 22.8), 120.3 (d, J = 6.6), 117.2 (d, J = 22.4), 21.2, 20.3. $^{19}$F NMR (376 MHz, CDCl$_3$, ref. C$_6$F$_6$): $\delta$ -121.8 (t, J = 8.0). IR (neat, cm$^{-1}$): 2916, 1650, 1438, 1316, 1201, 1093, 985, 882, 858, 797. HRMS (DART) m/z calculated for C$_{16}$H$_{15}$FO$_2$ $^{+}$ (M + H$^{+}$) 259.11288, found 259.11332.

5-Chloro-2',4',6'-trimethyl-[1,1'-biphenyl]-2-ol (SM6)

Following general procedure B, 2-bromo-4-chlorophenol (2.42 g, 11.7 mmol) was treated with sodium hydride (0.433 g, 17.1 mmol) in THF (24 ml), followed by addition of Pd(OAc)$_2$ (0.135 g, 0.588 mmol, 5.03 mol %), and mesitylmagnesium bromide (1 M, THF, 20 ml, 20.0 mmol) to give SM6 (1.11 g, 39 %) as a light beige powder. MP 77–80 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.23 (dd, J = 8.7, 2.6, 1H), 7.00 (d, J = 2.6, 1H), 6.99 (s, 2H), 6.93 (d, J = 8.7, 1H), 4.62 (s, 1H), 2.34 (s, 3H), 2.02 (s, 6H). $^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$): $\delta$ 151.3, 138.6, 137.7, 130.6, 129.7, 128.94, 128.90, 128.1, 125.4, 116.7, 21.2, 20.3. IR (neat, cm$^{-1}$): 3467, 3419, 2917, 1468, 1227, 1151, 852, 822, 714, 648. HRMS (DART) m/z calculated for C$_{15}$H$_{15}$ClO$^+$ (M$^+$) 246.08059, found 246.08109.

2-Hydroxy-5-chloro-2',4',6'-trimethyl-[1,1'-biphenyl]-3-carbaldehyde (SM7)

Following general procedure C, 5-chloro-2',4',6'-trimethyl-[1,1'-biphenyl]-2-ol (SM6, 1.00 g, 4.05 mmol) was treated with methylmagnesium bromide (1.5 ml, 4.6 mmol) in THF (8 ml), followed by addition of toluene (16 ml), triethylamine (0.9 ml, 6.5 mmol), and paraformaldehyde (0.334 g, 11.1 mmol). The product was purified via flash column chromatography (hexanes/EtOAc) to give SM7 (0.730 g, 66 %) as an off-white powder. MP 120–122 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 11.04 (s, 1H), 9.91 (s, 1H), 7.57 (d, J = 2.6, 1H), 7.32 (d, J = 2.6, 1H), 6.97 (s, 2H), 2.33 (s, 3H), 2.02 (s, 6H). $^{13}$C{$^1$H} NMR
(101 MHz, CDCl$_3$): $\delta$ 195.7, 157.6, 138.2, 138.0, 136.4, 132.3, 131.7, 131.5, 128.4, 124.6, 121.3, 21.2, 20.4. IR (neat, cm$^{-1}$): 2914, 1645, 1445, 1294, 1207, 1093, 852, 730. HRMS (DART) m/z calculated for C$_{16}$H$_{15}$ClO$_2^+$ (M + H$^+$) 275.08333, found 275.08377.
Synthesis of catalyst precursors to \((R)-1d-1f\)

Synthesis of \((R)-ML1\) (precursor to \((R)-1d\))

\((R)-3,3''-([1,1'-Binaphthalene]-2,2'-diylbis(azanylylidene))-bis(5-methoxy-2',4',6'-trimethyl-[1,1'-biphenyl]-2-ol) ((R)-pOMeMesBinam, (R)-L1)

Following general procedure D, 2-hydroxy-5-methoxy-2',4',6'-trimethyl-[1,1'-biphenyl]-3-carbaldehyde (SM3, 0.217 g, 0.803 mmol) was treated with \((R)-2,2'-diamine-1,1'-binaphthalene\) (0.114 g, 0.397 mmol) in methanol (2 ml). The filtered solid was recrystallized from toluene to give \((R)-L1\) (0.245 g, 78 %) as a dark orange powder. MP >200 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 11.66 (s, 2H), 8.23 (s, 2H), 7.98 (d, \(J = 8.7, 2H\)), 7.88 (d, \(J = 8.3, 2H\)), 7.38 (ddd, \(J = 8.1, 6.3, 1.6, 2H\)), 7.33 (d, \(J = 8.7, 2H\)), 7.18 (m, 4H), 6.92 (app s, 2H), 6.87 (app s, 2H), 6.69 (d, \(J = 3.0, 2H\)), 6.39 (d, \(J = 3.0, 2H\)), 3.67 (s, 6H), 2.29 (s, 6H), 2.05 (s, 6H), 1.86 (s, 6H). \(^{13}\)C\(^1\)H NMR (101 MHz, CDCl\(_3\)): δ 164.2, 152.3, 151.7, 146.2, 137.0, 136.4, 136.2, 133.9, 133.2, 132.3, 130.3, 129.9, 129.1, 128.4, 128.3, 128.1, 126.84, 126.81, 125.6, 121.8, 119.0, 118.4, 114.1, 55.5, 21.2, 20.5, 20.4. HRMS (DART) \(m/z\) calculated for C\(_{54}\)H\(_{48}\)N\(_2\)O\(_4\)\(^+\) (M + H\(^+\)) 789.36868, found 789.36633.
(R)-pOMeMesBinamAlCl  ((R)-ML1, (R)-pOMeMesBinam = (R)-3,3’-(((1,1’-Binaphthalene)-2,2’-diylbis(azanylylidene))bis(methanlylidene))bis(5-methoxy-2’,4’,6’-trimethyl-[1,1’-biphenyl]-2-olate))

General Procedure F was followed using Et₂AlCl (Aldrich, hexanes, 0.98 M, 265 µl, 0.260 mmol), (R)-3,3”-(((1,1’-binaphthalene)-2,2’-diylbis(azanylylidene))bis(methanlylidene))bis(5-methoxy-2’,4’,6’-trimethyl-[1,1’-biphenyl]-2-ol) ((R)-pOMeMesBinam, (R)-L1, 0.183 g, 0.232 mmol), and DCM (6 ml) to give (R)-pOMeMesBinamAlCl ((R)-ML1, 0.152 g, 76%) as a reddish-orange solid. MP >200 °C. ¹H NMR (500 MHz, CDCl₃, -55 °C): δ 8.41 (s, 1H), 8.27 (s, 1H), 8.04 (d, J = 8.6, 1H), 7.97 (d, J = 8.2, 1H), 7.92 (m, 2H), 7.62 (d, J = 8.5, 1H), 7.51 (m, 2H), 7.41 (d, J = 8.5, 1H), 7.30 (m, 2H), 7.12 (d, J = 8.4, 1H), 7.08 (s, 1H), 7.04 (d, J = 8.6, 1H), 6.97 (s, 1H), 6.89 (m, 2H), 6.89 (s, 1H), 6.76 (s, 1H), 6.61 (d, J = 2.9, 1H), 6.51 (d, J = 2.9, 1H), 3.67 (s, 3H), 3.64 (s, 3H), 2.45 (s, 3H), 2.37 (s, 3H), 2.05 (s, 3H), 1.91 (s, 3H), 1.88 (s, 3H), 1.62 (s, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃, -55 °C): δ 173.5, 168.9, 161.1, 156.5, 150.0, 149.6, 144.1, 143.9, 138.9, 137.7, 136.8, 136.2, 135.9, 135.4, 135.3, 134.6, 133.9, 133.6, 132.4, 132.2, 131.9, 130.0, 129.7, 129.5, 128.6, 128.2, 127.9, 127.8, 127.7, 127.6, 127.2, 127.1, 127.0, 126.9, 126.6, 126.34, 126.26, 126.2, 126.0, 125.6, 125.2, 118.1, 117.9, 113.1, 111.2, 55.6, 55.4, 21.6, 21.5, 21.4, 21.2, 20.4, 19.1. HRMS (DART) m/z calculated for C₅₄H₄₆AlClN₂O₄⁺ (M – Cl)⁺ 813.32675, found 813.32322.

Note: NMR spectra collected in CDCl₃ at 22 °C displayed very broad resonances. One ¹³C peak not observed due to pseudohomotopic aryl peaks.
Synthesis of \((R)\)-ML2 (precursor to \((R)\)-1e)

\((R)\)-3,3''-\(((1,1'\text{-Binaphthalene)}-2,2'\text{-diylbis(azanylylidene)})\text{bis(methanylylidene)})-\text{bis(5-fluoro-2',4',6'-trimethyl-[1,1'-biphenyl]-2-ol)}\ ((R)\text{-pFMesBinam}, \((R)\)-L2)

Following general procedure F, 2-hydroxy-5-fluoro-2',4',6'-trimethyl-[1,1'-biphenyl]-3-carbaldehyde (SM5, 0.207 g, 0.801 mmol) was treated with \((R)\)-2,2'-diamine-1,1'-binaphththalene (0.114 g, 0.395 mmol) in methanol (3 ml) to give \((R)\)-L2 (0.282 g, 92 %) as an orange powder. \textbf{MP >}200 °C. \textit{\textbf{1H NMR}} (400 MHz, CDCl\(_3\)): \(\delta\) 11.94 (s, 2H), 8.31 (s, 2H), 7.99 (d, \(J = 8.8\), 2H), 7.88 (d, \(J = 8.0\), 2H), 7.39 (m, 2H), 7.37 (d, \(J = 8.8\), 2H) 7.22 (m, 2H), 7.15 (app d, \(J = 8.4\), 2H), 6.91 (s, 2H), 6.87 (s, 2H), 6.81 (dd, \(J = 8.7\), 3.1, 2H), 6.69 (dd, \(J = 8.3\), 3.1, 2H), 2.29 (s, 6H), 1.96 (s, 6H), 1.81 (s, 6H). \textit{\textbf{13C\{\textit{1H}\} NMR}} (101 MHz, CDCl\(_3\)): \(\delta\) 162.9, 155.1 (d, \(J = 237.9\)), 154.3, 145.1, 137.3, 136.4, 136.3, 133.2, 133.1, 132.5, 130.5 (d, \(J = 7.1\)), 130.4, 128.4, 128.3, 128.2, 127.7, 127.0, 126.7, 125.9, 121.6 (d, \(J = 22.5\)), 119.0, 118.9, 118.2, 21.2, 20.3, 20.3. \textit{\textbf{19F NMR}} (376 MHz, CDCl\(_3\), ref. C\(_6\)F\(_6\)): \(\delta\) -124.3 (t, \(J = 8.4\)). \textbf{HRMS (DART)} \textit{m/z} calculated for C\(_{52}\)H\(_{42}\)F\(_2\)N\(_2\)O\(_2\)\(^+\) (M + H\(^+\)) 765.32871, found 765.32939.
(R)-pFMesBinamAlCl ((R)-ML2, (R)-pFMesBinam = (R)-3,3’’-((1,1’-Binaphthalene)-2,2’-diylbis(azanylylidene))bis(methanylylidene))bis(5-fluoro-2’,4’,6’-trimethyl-[1,1’-biphenyl]-2-olate))

General Procedure F was followed using Et2AlCl (Aldrich, hexanes, 0.98 M, 400 µl, 0.393 mmol), (R)-3,3’’-((1,1’-binaphthalene)-2,2’-diylbis(azanylylidene))bis(methanylylidene))bis(5-fluoro-2’,4’,6’-trimethyl-[1,1’-biphenyl]-2-ol) ((R)-pFMesBinam, (R)-L2, 0.265 g, 0.346 mmol), and DCM (10 ml) to give (R)-pFMesBinamAlCl ((R)-ML2, 0.214 g, 75 %) as an orange solid. MP >200 °C. ¹H NMR (500 MHz, CDCl₃, −55 °C): δ 8.40 (s, 1H), 8.22 (s, 1H), 8.04 (d, J = 8.5, 1H), 7.95 (m, 3H), 7.59 (d, J = 8.5, 1H), 7.52 (m, 2H), 7.38 (d, J = 8.5, 1H), 7.30 (m, 2H), 7.12 (d, J = 8.4, 1H), 7.07 (s, 1H), 7.05 (d, J = 8.7, 1H), 6.99 (m, 2H), 6.96 (s, 1H), 6.85 (m, 2H), 6.81 (dd, J = 8.0, 3.1, 1H), 6.77 (s, 1H), 2.44 (s, 3H), 2.38 (s, 3H), 2.02 (s, 3H), 1.88 (s, 3H), 1.84 (s, 3H), 1.58 (s, 3H).

¹³C{¹H} NMR (126 MHz, CDCl₃, −55 °C): δ 173.6, 168.4, 161.8, 157.8, 153.6 (d, J = 237.0), 153.2 (d, J = 236.1), 143.6, 143.5, 138.6, 137.4, 136.7, 136.5, 136.2, 135.8 (d, J = 7.3), 135.3, 134.4 (d, J = 6.6), 133.9, 133.0, 132.6, 132.3, 131.9, 131.8, 130.3, 129.7, 128.6, 128.2, 127.9, 127.7, 127.5, 127.3, 127.1, 126.59, 126.57, 126.11, 126.06, 125.9, 125.2, 125.1, 118.12, 118.05, 118.0, 116.9, 116.7, 116.2, 116.0, 21.45, 21.43, 21.37, 21.2, 20.3, 19.0. ¹⁹F NMR (470 MHz, CDCl₃, −55 °C, ref. C₆F₆): δ 125.25, 125.83. HRMS (DART) m/z calculated for C₅₂H₄₉AlClF₂N₂O₂⁺ (M−Cl)⁺ 789.28677, found 789.28306.

Note: NMR spectra collected in CDCl₃ at 22 °C displayed very broad resonances. One ¹³C peak not observed due to pseudohomotopic aryl peaks.
Synthesis of (R)-ML3 (precursor to (R)-1f)

(R)-3,3′′-(([1,1′-Binaphthalene]-2,2′-diylbis(azanylylidene))bis(methanylylidene))-bis(5-chloro-2′,4′,6′-trimethyl-[1,1′-biphenyl]-2-ol) ((R)-pClMesBinam, (R)-L3)

Following general procedure D, 2-hydroxy-5-chloro-2′,4′,6′-trimethyl-[1,1′-biphenyl]-3-carbaldehyde (SM7, 0.500 g, 1.92 mmol) was treated with (R)-2,2′-diamine-1,1′-binaphthalene (0.261 g, 0.910 mmol) in methanol (4.5 ml) to give (R)-L1 (0.684 g, 94 %) as a light orange powder. **MP >200 °C.** 1H NMR (400 MHz, CDCl3): δ 12.14 (s, 2H), 8.30 (s, 2H), 7.99 (d, J = 8.8, 2H), 7.88 (d, J = 8.2, 2H), 7.38 (m, 4H), 7.21 (m, 2H), 7.14 (d, J = 8.4, 2H), 7.01 (d, J = 2.6, 2H), 6.99 (d, J = 2.6, 2H), 6.90 (s, 2H), 6.86 (s, 2H), 2.29 (s, 6H), 1.94 (s, 6H), 1.80 (s, 6H). 13C{1H} NMR (101 MHz, CDCl3): δ 162.7, 156.7, 144.8, 137.3, 136.4, 136.3, 134.1, 133.2, 132.8, 132.5, 130.9, 130.4, 129.2, 128.39, 128.36, 128.3, 128.2, 127.1, 126.7, 125.9, 123.2, 120.0, 118.1, 21.2, 20.4, 20.3. HRMS (DART) m/z calculated for C52H42Cl2N2O2+ (M + H+) 797.26961, found 797.27019.
(R)-pClMesBinamAlCl ((R)-ML3, (R)-pClMesBinam = (R)-3,3''-([1,1'-Binaphthalene]-2,2'-diylbis(azanylylidene))bis(methanylylidene)bis(5-chloro-2',4',6'-trimethyl-[1,1'-biphenyl]-2-olate))

General Procedure F was followed using Et₂AlCl (Aldrich, hexanes, 0.98 M, 335 µl, 0.329 mmol, (R)-3,3''-([1,1'-binaphthalene]-2,2'-diylbis(azanylylidene))bis(methanylylidene)bis(5-chloro-2',4',6'-trimethyl-[1,1'-biphenyl]-2-olate) ((R)-pClMesBinam, (R)-L3, 0.231 g, 0.289 mmol), and DCM (7.5 ml) to give (R)-pClMesBinamAlCl ((R)-ML3, 0.185 g, 72 %) as a yellow solid. MP >200 °C. ¹H NMR (500 MHz, CDCl₃, -55 °C): δ 8.53 (s, 1H), 8.34 (s, 1H), 3.17 (d, J = 8.4, 1H), 8.08 (m, 3H), 7.69 (d, J = 8.5, 1H), 7.65 (m, 2H), 7.49 (d, J = 8.6, 1H), 7.43 (m, 2H), 7.39 (s, 1H), 7.29 (m, 1H), 7.26 (s, 1H), 7.24 (m, 2H), 7.20 (s, 1H), 7.17 (d, J = 8.7, 1H), 7.09 (s, 1H), 6.98 (s, 1H), 6.89 (s, 1H), 2.57 (s, 3H), 2.51 (s, 3H), 2.15 (s, 3H), 2.02 (s, 3H), 1.96 (s, 3H), 1.70 (s, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃, -55 °C): δ 173.6, 168.3, 163.6, 159.8, 143.4, 143.3, 138.9, 138.5, 137.9, 137.4, 136.7, 136.4, 136.0, 135.3, 134.7, 133.7, 132.7, 132.6, 132.3, 131.8, 131.7, 131.5, 131.4, 130.4, 129.7, 128.6, 128.2, 127.93, 127.91, 127.7, 127.3, 127.1, 127.0, 126.63, 126.58, 126.3, 126.0, 125.7, 125.0, 121.6, 120.9, 119.7, 119.5, 21.5, 21.42, 21.36, 21.2, 20.3, 19.1. HRMS (DART) m/z calculated for C₅₂H₄₀AlCl₅N₂O₂⁺ (M – Cl)⁺ 821.22767, found 821.22470.

Note: NMR spectra collected in CDCl₃ at 22 °C displayed very broad resonances. Two ¹³C peaks not observed due to pseudohomotopic aryl peaks.
Carbonylative desymmetrization of \textit{meso}-epoxides using \((R)-1b\)–\(f\)

\textbf{(3\textit{R},4\textit{R})-3,4-Dimethyloxetan-2-one (4b)}

Using \((R)-1b\):

General procedure F was followed using \((R)-\text{Xyl}_2\text{BinamAlCl}^5\) (precursor to \((R)-1b\), 4.8 mg, 0.0050 mmol, 2.5 mol %), \(\text{NaCo(CO)}_4\) (0.025 M, THF, 200 µl, 0.0050 mmol, 2.5 mol %) and \textit{meso}-(2\textit{R},3\textit{S})-2,3-dimethyloxirane (3\textit{b}, 14.3 mg, 0.198 mmol). The reaction mixture was stirred for 24 h at 22 °C. The volatility of 4\textit{b} interfered with its quantitative isolation, thus the yield of the reaction was determined using the method of standard addition. To this end, the crude reaction mixture was filtered through a short plug of silica gel using THF as eluent. The entire eluate was placed in a volumetric flask and diluted with THF to a total volume of 5 ml. A 0.5 ml aliquot of this solution was then analyzed via GC analysis. Additional 0.5 ml aliquots from this stock solution were subsequently treated with increasing amounts of independently isolated 4\textit{b}, and the resulting mixtures also analyzed via GC analysis. The observed increase in signal for 4\textit{b} was then used to determine that the yield of 4\textit{b} was approximately 18.7 mg (94 %).

Analytical data for 4\textit{b} has previously been reported.$^{11}$\textit{H} NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) 4.35 (qd, \(J = 6.1, 4.0, 1\text{H}\)), 3.22 (qd, \(J = 7.5, 4.0, 1\text{H}\)), 1.56 (d, \(J = 6.3, 3\text{H}\)), 1.39 (d, \(J = 7.7, 3\text{H}\)). \textit{C}{\textit{H}} NMR (126 MHz, CDCl\textsubscript{3}): \(\delta\) 171.9, 76.2, 52.3, 20.1, 12.4. \textbf{Specific rotation}: \([\alpha]^{22}_D = +43.7\) (\(c = 0.22, \text{CHCl}_3\)).

The enantiomeric ratio (er) was determined to be 91.3 : 8.7 by GC analysis (\(\beta\)-Dex225 column) in comparison to authentic \textit{racemic} material.
Using \((R)-1c\):

General procedure F was followed using \((R)-p\)MesMesBinamAlCl\(^5\) (precursor to \((R)-1c\), 0.025 M, THF, 400 µl, 0.010 mmol, 2.5 mol %), NaCo(CO)\(_4\) (0.025 M, THF, 400 µl, 0.010 mmol, 2.5 mol %) and \(meso-(2R,3S)-2,3\)-dimethyloxirane (3b, 28.7 mg, 0.398 mmol). After stirring at 22 °C for 24 h, the yield of 4b was determined as described above to be approximately 37.8 mg (95 %).

The enantiomeric ratio (er) was determined to be 91.5 : 8.5 by GC analysis (β-Dex120 column) in comparison to authentic racemic material.
Using (R)-1d:

General procedure F was followed using (R)-ML1 (precursor to (R)-1d, 5.9 mg, 0.0069 mmol, 4.2 mol %), NaCo(CO)$_4$ (1.3 mg, 0.0067 mmol, 4.1 mol %) and meso-(2R,3S)-2,3-dimethyloxirane (3b, 11.8 mg, 0.164 mmol). After stirring at 22 °C for 20 h, the reaction mixture was run through a plug of SiO$_2$ and analyzed by $^1$H NMR spectroscopy and chiral gas chromatography.

The enantiomeric ratio (er) was determined to be 93.0 : 7.0 by GC analysis (β-Dex225 column) in comparison to authentic racemic material.
Using (R)-1e:

General procedure F was followed using (R)-ML2 (precursor to (R)-1e, 5.7 mg, 0.0069 mmol, 4.4 mol %), NaCo(CO)$_4$ (2.7 mg, 0.014 mmol, 8.9 mol %) and meso-(2R,3S)-2,3-dimethyloxirane (3b, 11.3 mg, 0.157 mmol). After stirring at 22 °C for 20 h, the reaction mixture was run through a plug of SiO$_2$ and analyzed by $^1$H NMR spectroscopy and chiral gas chromatography.

The enantiomeric ratio (er) was determined to be 87.9 : 12.1 by GC analysis (β-Dex225 column) in comparison to authentic racemic material.
Using (R)-1f:

General procedure F was followed using (R)-ML3 (precursor to (R)-1f, 6.1 mg, 0.0071 mmol, 4.4 mol %), NaCo(CO)$_4$ (1.3 mg, 0.0067 mmol, 4.2 mol %) and meso-(2R,3S)-2,3-dimethyloxirane (3b, 11.6 mg, 0.161 mmol). After stirring at 22 °C for 20 h, the reaction mixture was run through a plug of SiO$_2$ and analyzed by $^1$H NMR spectroscopy and chiral gas chromatography.

The enantiomeric ratio (er) was determined to be 87.9 : 12.1 by GC analysis (β-Dex225 column) in comparison to authentic racemic material.
Stereochemical assignment of 4b:
The stereochemical identity of 4b was determined by two methods. First, the specific rotation of 4b was compared under identical conditions to that reported in the literature for (3S,4S)-3,4-dimethyloxetan-2-one\textsuperscript{11} and found to be of the opposite sign. Second, a racemic mixture of trans-3,4-dimethyloxetan-2-one was kinetically resolved to enantiopure (3R,4R)-3,4-dimethyloxetan-2-one by adapting a published procedure\textsuperscript{12} using Lipase PS and benzyl alcohol. The β-lactone isolated from this reaction was identical with 4b with regard to the sign of its specific rotation, and its GC retention time (Figures S1 and S2).

**Figure S1** GC trace (β-Dex225 column) of (3R,4R)-3,4-dimethyloxetan-2-one obtained from kinetic resolution using Lipase PS

**Figure S2** GC trace (β-Dex225 column) of isolated β-lactone 4b
(3R,4R)-3,4-Diethyloxetan-2-one (4c)

Using (R)-1b:

General procedure F was followed using (R)-Xyl$_2$BinamAlCl$_5$ (precursor to (R)-1b, 29.1 mg, 0.0300 mmol, 10.1 mol %), NaCo(CO)$_4$ (0.0500 M, THF, 600 µl, 0.0300 mmol, 10.1 mol %) and meso-(2R,3S)-2,3-diethyloxirane (3e, 29.8 mg, 0.298 mmol). After stirring at 22 °C for 24 h, the crude reaction mixture was subjected to bulb-to-bulb distillation to give 4c (28.2 mg, 74%) as a yellow oil. $^1$H NMR (400 MHz, CDCl$_3$): δ 4.17 (td, $J = 6.6, 3.9, 1$H), 3.12 (ddd, $J = 8.5, 6.5, 4.0, 1$H), 1.93–1.69 (m, 4H), 1.02 (t, $J = 7.5, 3$H), 0.99 (t, $J = 7.4, 3$H). $^{13}$C($^1$H) NMR (75 MHz, CDCl$_3$): δ 171.5, 78.8, 57.2, 27.6, 21.2, 11.4, 9.2. IR (neat, cm$^{-1}$): 2969, 2939, 2880, 1812, 1461, 1386, 1120, 1062, 954. HRMS (ESI) m/z calculated for C$_7$H$_{13}$O$_2$ ($\text{M + H}^+$) 129.0916, found 129.0922. Specific rotation: $[\alpha]_{22}^{22}$ = +23.6 ($c = 0.51$, CHCl$_3$).

The enantiomeric ratio (er) was determined to be 99.0 : 1.0 by GC analysis (β-Dex225 column) in comparison to authentic racemic material.

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Using (R)-1c:

General procedure F was followed using (R)-pMeMesBinamAlCl\(^5\) (precursor to (R)-1c, 8.2 mg, 0.010 mmol, 3.9 mol %), NaCo(CO)\(_4\) (0.0500 M, THF, 200 µl, 0.0100 mmol, 3.91 mol %) and meso-(2R,3S)-2,3-diethylxirane\(^7\) (3c, 1.28 M, THF, 200 µl, 0.256 mmol). After stirring at 22 °C for 24 h, the crude reaction mixture was subjected to bulb-to-bulb distillation to give 4c (23.0 mg, 70 %) as a yellow oil.

The enantiomeric ratio (er) was determined to be 97.8 : 2.2 by GC analysis (β-Dex120 column) in comparison to authentic racemic material.
Using (R)-1d:

General procedure F was followed using (R)-ML1 (precursor to (R)-1d, 5.9 mg, 0.0069 mmol, 5.4 mol%), NaCo(CO)$_4$ (1.4 mg, 0.0072 mmol, 5.6 mol%) and meso-(2R,3S)-2,3-diethyloxirane$^7$ (3c, 12.9 mg, 0.129 mmol). After stirring at 22 °C for 20 h, the reaction mixture was run through a plug of SiO$_2$ and analyzed by $^1$H NMR spectroscopy and chiral gas chromatography.

The enantiomeric ratio (er) was determined to be 97.6 : 2.4 by GC analysis (β-Dex225 column) in comparison to authentic racemic material.
Using (R)-1e:

General procedure F was followed using (R)-ML2 (precursor to (R)-1e, 5.8 mg, 0.0070 mmol, 3.9 mol %), NaCo(CO)$_4$ (1.5 mg, 0.0077 mmol, 4.3 mol %) and meso-(2R,3S)-2,3-diethyloxirane$^7$ (3c, 17.9 mg, 0.179 mmol). After stirring at 22 °C for 20 h, the reaction mixture was run through a plug of SiO$_2$ and analyzed by $^1$H NMR spectroscopy and chiral gas chromatography.

The enantiomeric ratio (er) was determined to be 98.2 : 1.8 by GC analysis (β-Dex225 column) in comparison to authentic racemic material.
Using (R)-1f:

General procedure F was followed using (R)-ML3 (precursor to (R)-1f, 6.4 mg, 0.0075 mmol, 4.7 mol %), NaCo(CO)₄ (1.3 mg, 0.0067 mmol, 4.2 mol %) and meso-(2R,3S)-2,3-dieyloxyrane⁷ (3c, 15.9 mg, 0.159 mmol). After stirring at 22 °C for 20 h, the reaction mixture was run through a plug of SiO₂ and analyzed by ¹H NMR spectroscopy and chiral GC.

The enantiomeric ratio (er) was determined to be 98.5 : 1.5 by GC analysis (β-Dex225 column) in comparison to authentic racemic material.

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Stereochemical assignment of 4c:
The stereochemical identity of 4c was determined by comparing the order of elution of the two enantiomers during GC analysis with that of 4b and 4a.

(3R,4R)-3,4-Dipropoxetan-2-one (4a)

Using (R)-1b:

General procedure F was followed using (R)-Xyl₂BinamAlCl⁵ (precursor to (R)-1b, 9.7 mg, 0.010 mmol, 10 mol %), NaCo(CO)₄ (1.00 M, THF, 100 µl, 0.0100 mmol, 10.0 mol %) and meso-(2R,3S)-2,3-dipropoxirane⁶ (3a, 1.00 M, THF, 100 µl, 0.100 mmol). After
stirring at 22 °C for 24 h, the crude reaction mixture was subjected to bulb-to-bulb distillation to give 4a (11.9 mg, 76 %) as a yellow oil. Analytical data for 4a has previously been reported.\textsuperscript{13} \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta 4.22\) (ddd, \(J = 7.4, 5.9, 4.0, 1H\)), 3.17 (ddd, \(J = 8.8, 6.6, 4.0, 1H\)), 1.88–1.77 (m, 2H), 1.75–1.64 (m, 2H), 1.51–1.37 (m, 4H), 0.97 (t, \(J = 7.4, 3H\)), 0.94 (t, \(J = 7.3, 3H\)). \textsuperscript{13}C\{\textsuperscript{1}H\} NMR (126 MHz, CDCl\textsubscript{3}): \(\delta 171.7, 78.1, 56.1, 36.6, 30.1, 20.4, 18.5, 13.86, 13.86\). Specific rotation: \(\left[\alpha\right]_{D}^{22} = +30.3\) (\(c = 1.29, \text{CHCl}_{3}\)).

The enantiomeric ratio (er) was determined to be 98.6 : 1.4 by GC analysis (\(\beta\)-Dex120 column) in comparison to authentic racemic material.

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Using (R)-1c:
General procedure F was followed using (R)-pMeMesBinamAlCl\(^5\) (precursor to (R)-1c, 14.3 mg, 0.0175 mmol, 7.00 mol %), NaCo(CO)\(_4\) (0.100 M, THF, 175 µl, 0.0175 mmol, 7.00 mol %) and meso-(2R,3S)-2,3-dipropylxirane\(^6\) (3a, 1.00 M, THF, 250 µl, 0.250 mmol). After stirring at 22 °C for 24 h, the crude reaction mixture was subjected to bulb-to-bulb distillation to give 4a (30.1 mg, 77 %) as a yellow oil.

The enantiomeric ratio (er) was determined to be 96.9 : 3.1 by GC analysis (β-Dex120 column) in comparison to authentic racemic material.

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Using (R)-1d:
General procedure F was followed using (R)-ML1 (precursor to (R)-1d, 5.9 mg, 0.0069 mmol, 5.0 mol %), NaCo(CO)\(_4\) (1.5 mg, 0.0077 mmol, 5.6 mol %) and meso-(2R,3S)-2,3-dipropylxirane\(^6\) (3a, 17.7 mg, 0.138 mmol). After stirring at 22 °C for 20 h, the reaction mixture was run through a plug of SiO\(_2\) and analyzed by \(^1\)H NMR spectroscopy and chiral GC.

The enantiomeric ratio (er) was determined to be 96.0 : 4.0 by GC analysis (β-Dex225 column) in comparison to authentic racemic material.
Using (R)-1e:

General procedure F was followed using (R)-ML2 (precursor to (R)-1e, 5.8 mg, 0.0070 mmol, 5.4 mol %), NaCo(CO)₄ (2.3 mg, 0.012 mmol, 9.2 mol %) and meso-(2R,3S)-2,3-dipropoxyxirane⁶ (3a, 16.5 mg, 0.129 mmol). After stirring at 22 °C for 20 h, the reaction mixture was run through a plug of SiO₂ and analyzed by ¹H NMR spectroscopy and chiral GC.

The enantiomeric ratio (er) was determined to be 97.0 : 3.0 by GC analysis (β-Dex225 column) in comparison to authentic racemic material.
Using (R)-1f:

General procedure F was followed using (R)-**ML3** (precursor to (R)-**1f**, 6.1 mg, 0.0071 mmol, 5.4 mol %), NaCo(CO)$_4$ (1.6 mg, 0.0082 mmol, 6.3 mol %) and meso-(2R,3S)-2,3-dipropoxirane$^6$ (**3a**, 16.9 mg, 0.132 mmol). After stirring at 22 °C for 20 h, the reaction mixture was run through a plug of SiO$_2$ and analyzed by $^1$H NMR spectroscopy and chiral GC.

The enantiomeric ratio (er) was determined to be 97.9 : 2.1 by GC analysis (**β**-Dex225 column) in comparison to authentic racemic material.
Stereochemical assignment of 4a:
The stereochemical identity of 4a was determined by comparing the specific rotation of 4a under identical conditions to that reported in the literature for (3R,4R)-3,4-dipropyl-oxetan-2-one. The literature known compound (95 % ee, $[\alpha]^{22}_{\text{D}} = +36.8$ ($c = 1.630$, CHCl$_3$)) and 4a (97 % ee, $[\alpha]^{22}_{\text{D}} = +30.3$ ($c = 1.29$, CHCl$_3$)) displayed the same sign and approximately the same magnitude of rotation.

(3R,4R)-3,4-Dibutylxetan-2-one (4d)

Using ($R$)-1b:
General procedure F was followed using ($R$)-Xyl$_2$BinamAlCl$_5$ (precursor to ($R$)-1b, 23.3 mg, 0.0240 mmol, 12.1 mol %), NaCo(CO)$_4$ (0.120 M, THF, 200 µl, 0.0240 mmol, 12.1 mol %) and meso-(2R,3S)-2,3-dibutylxirane (3d, 0.994 M, THF, 200 µl, 0.199 mmol). After stirring at 22 °C for 24 h, the crude reaction mixture was subjected to bulb-to-bulb distillation to give 4d (26.4 mg, 72 %) as a yellow oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 4.20 (ddd, $J = 7.4$, 6.0, 4.0, 1H), 3.15 (ddd, $J = 8.7$, 6.6, 3.9, 1H), 1.89–1.65 (m, 4H), 1.44–1.29 (m, 8H), 0.91 (t, $J = 7.0$, 3H), 0.90 (t, $J = 7.0$, 3H). $^{13}$C{$^1$H} NMR (75 MHz, CDCl$_3$): $\delta$ 171.8, 78.3, 56.2, 34.2, 29.2, 27.2, 27.2, 22.50, 22.46, 14.0, 13.9. IR (neat, cm$^{-1}$): 2957, 2931, 2861, 1817, 1466, 1125, 1064, 838. HRMS (ESI) $m/z$ calculated for C$_{11}$H$_{21}$O$_2^+$ (M + H$^+$) 185.1542, found 185.1543. Specific rotation: $[\alpha]^{22}_{\text{D}} = +25.0$ ($c = 0.76$, CHCl$_3$).

The enantiomeric ratio (er) was determined to be 95.6 : 4.4 by GC analysis ($\beta$-Dex225 column) in comparison to authentic racemic material.
Using (R)-1c:

General procedure F was followed using (R)-pMeMesBinamAlCl\textsuperscript{5} (precursor to (R)-1c, 13.1 mg, 0.0160 mmol, 8.04 mol %), NaCo(CO)\textsubscript{4} (0.0800 M, THF, 200 µl, 0.0160 mmol, 8.00 mol %) and meso-(2R,3S)-2,3-dibutylloxirane\textsuperscript{8} (3d, 0.994 M, THF, 200 µl, 0.199 mmol). After stirring at 22 °C for 24 h, the crude reaction mixture was subjected to bulb-to-bulb distillation to give 4d (26.7 mg, 72 %) as a yellow oil.

The enantiomeric ratio (er) was determined to be 95.9 : 4.1 by GC analysis (β-Dex120 column) in comparison to authentic racemic material.
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2 | 63.666 | MM | 0.2295 | 192.31415 | 13.96905 | 49.94204

--- | --- | --- | --- | --- | --- | ---
1 | 62.081 | MM | 0.2552 | 412.22443 | 26.91874 | 95.91271
2 | 63.686 | MM | 0.2309 | 17.55688 | 1.2679 | 4.08729

Using (R)-1d:

General procedure F was followed using (R)-ML1 (precursor to (R)-1d, 5.9 mg, 0.0069 mmol, 4.6 mol %), NaCo(CO)$_4$ (1.5 mg, 0.0077 mmol, 5.1 mol %) and meso-(2R,3S)-2,3-dibutyloxirane$^8$ (3d, 23.5 mg, 0.150 mmol). After stirring at 22 °C for 20 h, the reaction mixture was run through a plug of SiO$_2$ and analyzed by $^1$H NMR spectroscopy and chiral GC.

The enantiomeric ratio (er) was determined to be 95.0:5.0 by GC analysis (β-Dex225 column) in comparison to authentic racemic material.
--- | --- | --- | --- | --- | --- | ---
1 | 41.635 | MM | 0.3793 | 190.40520 | 8.36624 | 50.12667
2 | 43.484 | MM | 0.4239 | 189.44292 | 7.44791 | 49.87333

--- | --- | --- | --- | --- | --- | ---
1 | 41.567 | MM | 0.4277 | 297.46405 | 11.59227 | 94.97985
2 | 43.907 | MM | 0.3530 | 15.72243 | 7.42406e-1 | 5.02015

Using \((R)-1\)

General procedure F was followed using \((R)-ML2\) (precursor to \((R)-1\), 5.8 mg, 0.0070 mmol, 4.6 mol %), NaCo(CO)$_4$ (1.5 mg, 0.0077 mmol, 5.0 mol %) and \textit{meso-\text{\text{\text{2R,3S}}}2,3\text{-dibutyloxirane}}\(^\text{8}\) (3d, 24.0 mg, 0.154 mmol). After stirring at 22 °C for 20 h, the reaction mixture was run through a plug of SiO$_2$ and analyzed by $^1$H NMR spectroscopy and chiral GC.

The enantiomeric ratio (er) was determined to be 96.5 : 3.5 by GC analysis (\(\beta\)-Dex225 column) in comparison to authentic \textit{racemic} material.
Using (R)-1f:

General procedure F was followed using (R)-ML3 (precursor to (R)-1f, 5.9 mg, 0.0069 mmol, 3.7 mol %), NaCo(CO)₄ (1.5 mg, 0.0077 mmol, 4.2 mol %) and meso-(2R,3S)-2,3-dibutoxirane₈ (3d, 28.8 mg, 0.184 mmol). After stirring at 22 °C for 20 h, the reaction mixture was run through a plug of SiO₂ and analyzed by ¹H NMR spectroscopy and chiral GC.

The enantiomeric ratio (er) was determined to be 97.9 : 2.1 by GC analysis (β-Dex225 column) in comparison to authentic racemic material.

Stereochemical assignment of 4d:

The stereochemical identity of 4d was determined by comparing the order of elution of the two enantiomers during GC analysis with that of 4b and 4a.
(3R,4R)-3,4-Bis(3-(2,2,2-trifluoroethoxy)propyl)oxetan-2-one (4e)

General procedure F was followed using (R)-pMeMesBinamAlCl5 (precursor to (R)-1c, 25.5 mg, 0.0312 mmol, 12.5 mol %), NaCo(CO)4 (0.0624 M, THF, 500 µl, 0.0312 mmol, 12.5 mol %) and meso-2,3-bis(3-(2,2,2-trifluoroethoxy)propyl)oxirane (3e, 80.4 mg, 0.248 mmol). After stirring at 33 °C for 24 h, the crude reaction mixture was subjected to flash column chromatography to give 4e (68.6 mg, 79 %) as a yellow oil. 1H NMR (300 MHz, CDCl3): δ 4.39 (td, J = 6.6, 4.1, 1H), 3.81 (qd, J = 8.7, 2.5, 4H), 3.70–3.60 (m, 4H), 3.25 (td, J = 7.6, 4.0, 1H), 1.98–1.65 (m, 8H). 13C{1H} NMR (75 MHz, CDCl3): δ 171.1, 124.0 (q, J = 279.6), 77.7, 72.02, 71.95, 68.45 (q, J = 34.0), 68.44 (q, J = 34.0), 55.9, 31.2, 27.0, 25.4, 24.7. Note: The two CF3-groups are pseudohomotopic, thus only one signal was observed. 19F NMR (376 MHz, CDCl3, ref. CFCl3): δ -74.3 (td, J = 8.9, 2.6). IR (neat, cm⁻¹): 2923, 2853, 1816, 1445, 1275, 1121, 966, 826. HRMS (ESI) m/z calculated for C13H19F6O4+ (M + H+) 353.1182, found 353.1197. Specific rotation: [α]22D = +19.8 (c = 1.52, CHCl3).

The enantiomeric ratio (er) was determined to be 92.0 : 8.0 by GC analysis (β-Dex225 column) in comparison to authentic racemic material.

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Stereochemical assignment of 4e:

The stereochemical identity of 4e was determined by comparing the order of elution of the two enantiomers during GC analysis with that of 4a–d.
Carbonylative desymmetrization of meso-epoxides using (R)-1d or (R)-1f at 0 °C

(3R,4R)-3,4-Dimethyloxetan-2-one (4b)

General procedure G was followed using (R)-ML1 (precursor to (R)-1d, 5.0 mg, 0.0059 mmol, 3.3 mol %), NaCo(CO)₄ (1.5 mg, 0.0077 mmol, 4.3 mol %) and meso-(2R,3S)-2,3-dimethyloxirane (3b, 12.9 mg, 0.179 mmol).

The enantiomeric ratio (er) was determined to be 93.9 : 6.1 by GC analysis (β-Dex120 column) in comparison to authentic racemic material.
General procedure G was followed using (R)-ML3 (precursor to (R)-1f, 6.3 mg, 0.0073 mmol, 4.6 mol %), NaCo(CO)$_4$ (1.5 mg, 0.0077 mmol, 4.9 mol %) and meso-(2R,3S)-2,3-diethyloxirane$^7$ (3c, 15.9 mg, 0.159 mmol).

The enantiomeric ratio (er) was determined to be 98.8 : 1.2 by GC analysis (β-Dex225 column) in comparison to authentic racemic material.
(3R,4R)-3,4-Dipropyloxetan-2-one (4a)

General procedure G was followed using (R)-ML3 (precursor to (R)-1f, 6.5 mg, 0.0076 mmol, 5.2 mol %), NaCo(CO)$_4$ (1.7 mg, 0.0088 mmol, 6.0 mol %) and meso-(2R,3S)-2,3-dipropyloxirane$^6$ (3a, 18.6 mg, 0.145 mmol).

The enantiomeric ratio (er) was determined to be 98.3 : 1.7 by GC analysis ($\beta$-Dex225 column) in comparison to authentic racemic material.

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(3R,4R)-3,4-Dibutylloxetan-2-one (4d)

General procedure G was followed using (R)-ML3 (precursor to (R)-1f, 6.4 mg, 0.0075 mmol, 4.8 mol %), NaCo(CO)$_4$ (1.8 mg, 0.0093 mmol, 6.0 mol %) and meso-(2R,3S)-2,3-dibutylloxirane$^8$ (3d, 24.1 mg, 0.154 mmol).

The enantiomeric ratio (er) was determined to be 98.5 : 1.5 by GC analysis (β-Dex225 column) in comparison to authentic racemic material.

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References

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

(Z)-1,8-Bis(2,2,2-trifluoroethoxy)oct-4-ene (SM1), $^1\text{H}$ NMR spectrum (400 MHz, CDCl$_3$)

$^{13}\text{C}[^1\text{H}]$ NMR spectrum (101 MHz, CDCl$_3$)
$^1$H NMR spectrum (376 MHz, CDCl$_3$)
2,3-Bis(3-(2,2,2-trifluoroethoxy)propyl)oxirane (3e), $^1$H NMR spectrum (400 MHz, C$_6$D$_6$)

$^{13}$C($^1$H) NMR spectrum (101 MHz, C$_6$D$_6$)
$^{19}$F NMR spectrum (376 MHz, $C_6D_6$)
5-Methoxy-2',4',6'-trimethyl-[1,1'-biphenyl]-2-ol (SM2), \(^1\)H NMR spectrum (400 MHz, CDCl\(_3\))

\(^{13}\)C\{\(^1\)H\} NMR spectrum (101 MHz, CDCl\(_3\))
2-Hydroxy-5-methoxy-2',4',6'-trimethyl-[1,1'-biphenyl]-3-carbaldehyde (SM3), $^1$H NMR spectrum (400 MHz, CDCl$_3$)

$^{13}$C($^1$H) NMR spectrum (101 MHz, CDCl$_3$)
5-Fluoro-2',4',6'-trimethyl-[1,1'-biphenyl]-2-ol (SM4), $^1$H NMR spectrum (400 MHz, CDCl$_3$)

$^{13}$C($^1$H) NMR spectrum (126 MHz, CDCl$_3$)
$^{19}\text{F NMR spectrum}$ (376 MHz, CDCl$_3$, ref. C$_6$F$_6$)
2-Hydroxy-5-fluoro-2',4',6'-trimethyl-[1,1'-biphenyl]-3-carbaldehyde (SM5), $^1$H NMR spectrum (400 MHz, CDCl$_3$)

$^{13}$C($^1$H) NMR spectrum (126 MHz, CDCl$_3$)
$^{19}$F NMR spectrum (376 MHz, CDCl$_3$, ref. C$_6$F$_6$)
5-Chloro-2',4',6'-trimethyl-[1,1'-biphenyl]-2-ol (SM6), $^1$H NMR spectrum (400 MHz, CDCl$_3$)

$^{13}$C ($^1$H) NMR spectrum (101 MHz, CDCl$_3$)
2-Hydroxy-5-chloro-2',4',6'-trimethyl-[1,1'-biphenyl]-3-carbaldehyde (SM7), $^1$H NMR spectrum (400 MHz, CDCl$_3$)

$^{13}$C($^1$H) NMR spectrum (101 MHz, CDCl$_3$)
(R)-pOMeMesBinam ((R)-L1), $^1$H NMR spectrum (400 HHz, CDCl$_3$)

$^{13}$C($^1$H) NMR spectrum (101 MHz, CDCl$_3$)
(R)-pOMesBinamAlCl ((R)-ML1, precursor to (R)-1d), $^1$H NMR spectrum (500 MHz, CDCl$_3$, −55 °C)

$^{13}$C{$^1$H} NMR spectrum (126 MHz, CDCl$_3$, −55 °C)
$^1$H NMR spectrum (400 MHz, CDCl$_3$, 22 °C)
(R)-pFMesBinam ((R)-L2), $^1$H NMR spectrum (400 MHz, CDCl$_3$)

$^{13}$C($^1$H) NMR spectrum (101 MHz, CDCl$_3$)
$^{19}$F NMR spectrum (376 MHz, CDCl$_3$, ref. C$_6$F$_6$)
(R)-pFMesBinamAlCl ((R)-ML2, precursor to (R)-1e), $^1$H NMR spectrum (500 MHz, CDCl$_3$, $-55$ °C)

$^{13}$C{$^1$H} NMR spectrum (126 MHz, CDCl$_3$, $-55$ °C)
$^1$H NMR spectrum (400 MHz, CDCl$_3$, 22 °C)

$^{19}$F NMR spectrum (470 MHz, CDCl$_3$, −55 °C, ref. C$_6$F$_6$)
(R)-pClMesBinam (R)-L3, $^1$H NMR spectrum (400 HHz, CDCl$_3$)

$^{13}$C($^1$H) NMR spectrum (101 MHz, CDCl$_3$)
(R)-pClMesBinamAlCl ((R)-ML3, precursor to (R)-1f), $^1$H NMR spectrum (500 MHz, CDCl$_3$, −55 °C)

$^{13}$C{$^1$H} NMR spectrum (126 MHz, CDCl$_3$, −55 °C)
$^1$H NMR spectrum (400 MHz, CDCl$_3$, 22 °C)
(3R,4R)-3,4-Dimethyloxetan-2-one (4b), $^1$H NMR spectrum (400 MHz, CDCl$_3$)

$^{13}$C($^1$H) NMR spectrum (126 MHz, CDCl$_3$)
(3R,4R)-3,4-Diethyloxetan-2-one (4c), $^1$H NMR spectrum (400 MHz, CDCl$_3$)

$^{13}$C($^1$H) NMR spectrum (75 MHz, CDCl$_3$)
(3R,4R)-3,4-Dipropylxetan-2-one (4a), $^1$H NMR spectrum (400 MHz, CDCl$_3$)

$^{13}$C($^1$H) NMR spectrum (126 MHz, CDCl$_3$)
(3R,4R)-3,4-Dibutylacetan-2-one (4d), $^1$H NMR spectrum (400 MHz, CDCl$_3$)

$^{13}$C($^1$H) NMR spectrum (75 MHz, CDCl$_3$)
(3R,4R)-3,4-Bis(3-(2,2,2-trifluoroethoxy)propyl)oxetan-2-one (4e). $^1$H NMR spectrum (300 MHz, CDCl₃)

$^{13}$C-$^1$H NMR spectrum (75 MHz, CDCl₃)
$^{19}$F NMR spectrum (376 MHz, CDCl$_3$)