

## Supporting Information

### **Stereoselective synthesis of trisubstituted epoxides via cobalt catalysis.**

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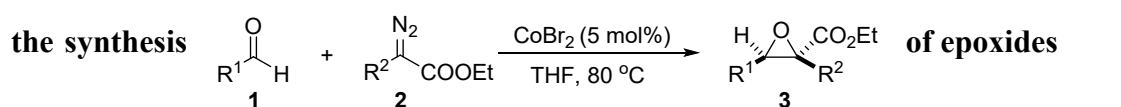
## 1. General Information

All reactions were carried out under an atmosphere of nitrogen in flame-dried sealed tube with magnetic stirring.  $^1\text{H}$  NMR spectra,  $^{13}\text{C}$  {H} NMR spectra,  $^{19}\text{F}$  NMR spectra were recorded on a Bruker 400 MHz spectrometer in  $\text{CDCl}_3$ . All signals are reported in  $\delta$  units, parts per million (ppm), and were referenced to  $\text{CDCl}_3$  ( $\delta$  7.26 ppm for  $^1\text{H}$  NMR and 77.0 ppm for  $^{13}\text{C}$  {H} NMR) as the internal standard. Data for  $^1\text{H}$  NMR spectra are reported as follows: chemical shift (ppm; s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet), coupling constant (Hz), and integration. Data for  $^{13}\text{C}$  {H} NMR are reported in terms of chemical shift (ppm) relative to residual solvent peak ( $\text{CDCl}_3$ : 77.0 ppm). HRMS spectra were recorded on GCQTOF 7200. MP data were recorded on WRS-2. Reactions were monitored by thin layer chromatography (TLC) using silica gel plates. Flash column chromatography was performed over silica gel (300-400 mesh ASTM, purchased from Yantai, China).

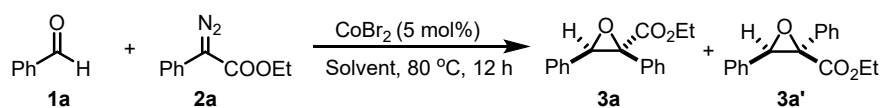
**Materials.** Unless otherwise noted, commercial reagents were purchased from Energy chemical, Bidepharm, Aesar, and other commercial suppliers and were used as received. Dioxane was freshly distilled from  $\text{CaH}_2$ . THF was freshly distilled from sodium metal prior to use. Diazo esters were prepared according to the literature procedures.<sup>1-3</sup>

## 2. Detailed Optimization of Reaction Conditions

### 2.1 General



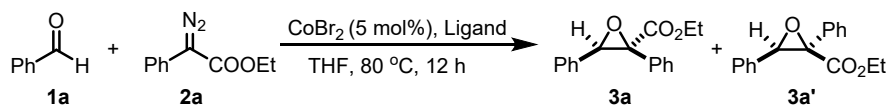
Under Ar atmosphere, to a 10 mL over-dried tube was charged with a stir bar and  $\text{CoBr}_2$  (5 mol%, 3.3 mg). THF (1.5 mL) and aldehyde **1** (0.3 mmol, 1.0 equiv) was injected into the tube by syringe and stirred for 10 mins in the glovebox, then diazoester **2** (0.36 mmol, 1.2 equiv) was injected into the tube by syringe. The resultant solution was stirred at 80 °C for 24 hours (monitored by TLC). After the reaction is complete, the solution was concentrated under vacuum and the obtained residue was purified by flash column chromatography on silica gel (petroleum ether and ethyl acetate as eluents, the ratio is from 50:1 to 10:1) to afford epoxide **3**.

**Table S1. Screening of Solvent<sup>a</sup>**

Entry	Solvent	Yield (3a)(%) <sup>b</sup>	Yield (3a')(%) <sup>b</sup>	Conv (1a)(%)
1	DCE	32	32	73
2	DCM	30	11	57
3	DMSO	N.R	N.R	42
4	DMF	N.R	N.R	63
5	DMAC	N.R	N.R	48
6	NMP	N.R	N.R	20
7	Cyclohexane	trace	trace	20
8	<i>n</i> -Hexane	trace	trace	41
9	Dioxide	trace	trace	20
10	DME	trace	trace	41
11	MTBE	trace	trace	8
12	Isopropyl ether	trace	trace	10
13	EA	trace	trace	2
14	Toluene	26	8	60
15	$\text{PhCF}_3$	38	10	63
16	MeCN	83	4	91
17	THF	90	3	99
18	2-MeTHF	N.R	N.R	18

a: Reaction condition: **1a** (0.2 mmol), **2a** (0.3 mmol),  $\text{CoBr}_2$  (10 mol%), Solvent (1 mL), stirred in 80 °C for 12 h under nitrogen atmosphere b: Detected by GC using mesitylene as an internal standard

**Table S2. Screening of Ligands<sup>a</sup>**



Entry	Ligand	Yield ( <b>3a</b> )(%) <sup>b</sup>	Yield ( <b>3a'</b> )(%) <sup>b</sup>	Conv ( <b>1a</b> )(%)
1	XPhos	67	trace	74
2	Ph-XPhos	71	trace	76
3	Ruphos	4	trace	6
4	dppe	50	trace	63
5	dppp	75	trace	85
6	dppb	74	trace	75
7	dppf	47	trace	57
8	dppm	54	trace	62
9	dpephos	75	trace	78
10	Xantphos	29	trace	31
11	BINAP	60	trace	80
12 <sup>c</sup>	$\text{PPh}_3$	57	trace	85
13 <sup>cd</sup>	$\text{P}^t\text{Bu}_3 \cdot \text{HBF}_4$	86	trace	87
14 <sup>c</sup>	$\text{PCy}_3$	10	trace	24

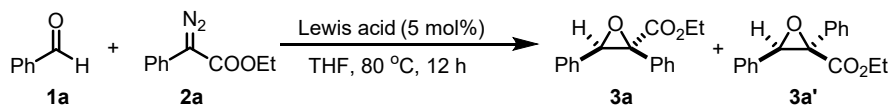
a: Reaction condition: a mixture of **1a** (0.2 mmol), **2a** (0.3 mmol) and mesitylene (10  $\mu\text{L}$ ) in THF (0.5 mL) solution was stirred for 10 min in room temperature.  $\text{CoBr}_2$  (10 mol%) and ligand (12 mol%) was stirred in THF (0.5 mL) for 10 min in room temperature. Then pouring the substrate into the complex solution by the syringe, stirred in 80 °C for 12 h

b: Detected by GC using mesitylene as an internal standard

c: 20 mol% Ligand

d: 20 mol%  $\text{K}_2\text{CO}_3$

**Table S3. Screening of Lewis acids<sup>a</sup>**

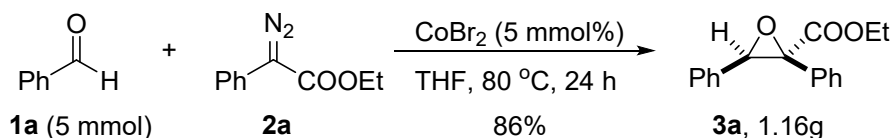


Entry	Ligand	Yield (3a)(%) <sup>b</sup>	Yield (3a')(%) <sup>b</sup>	Conv (1a)(%)
1	ZnCl <sub>2</sub>	NR	NR	< 1
2	MgCl <sub>2</sub>	NR	NR	< 1
3	InCl <sub>3</sub>	NR	NR	< 1
4	AlCl <sub>3</sub>	NR	NR	< 1
5	FeCl <sub>3</sub>	NR	NR	< 1
6	BF <sub>3</sub> ·Et <sub>2</sub> O	NR	NR	< 1
7	NiBr <sub>2</sub>	NR	NR	23
8	NiI <sub>2</sub>	NR	NR	25
9	Ni(COD) <sub>2</sub>	NR	NR	< 1
10	Ni(PPh <sub>3</sub> ) <sub>4</sub>	NR	NR	< 1

a: Reaction condition: a mixture of **1a** (0.2 mmol), **2a** (0.3 mmol) and mesitylene (10 μL) in THF (0.5 mL) solution was stirred for 10 min in room temperature. Lewis acid (10 mol%) was stirred in THF (0.5 mL) for 10 min in room temperature. Then pouring the substrate into the complex solution by the syringe, stirred in 80 °C for 12 h.

b: Detected by GC using mesitylene as an internal standard

### 3.

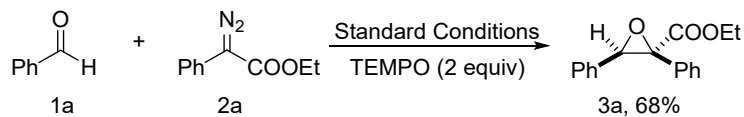


## Gram-scale Reaction

Under Ar atmosphere, to a 100 mL over-dried Schlenk tube was charged with a stir bar and CoBr<sub>2</sub> (5 mol%, 55 mg). THF (30 mL) and benzaldehyde **1a** (0.53 g, 5 mmol,) was injected into the tube by syringe and stirred for 10 mins in the glovebox, then diazoester **2a** (1.14 g, 6 mmol,) was injected into the tube by syringe. The resultant solution was stirred at 80 °C for 24 hours (monitored by TLC). After the reaction is complete, the solution was concentrated under vacuum and the obtained residue was purified by flash column chromatography on silica gel (petroleum ether and ethyl acetate as eluents, the ratio is 50:1) to afford oxirane **3a** (1.16 g, 86%).

## 4. Control Experiments

### 4.1



TEMPO

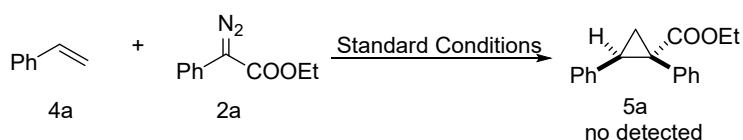
Trapping

Experiment

Under Ar atmosphere, to a 10 mL over-dried tube was charged with a stir bar and CoBr<sub>2</sub> (5 mol%, 3.3 mg). THF (1.5 mL) and benzaldehyde (xxx mg, 0.3 mmol, 1.0 equiv), TEMPO (xxx mg, 0.6 mmol, 2 equiv) was added into the tube and stirred for 10 mins in the glovebox, then diazoester **2a** (0.36 mmol, 1.2 equiv.) was injected into the tube by syringe. The resultant solution was stirred at 80 °C for 24 hours (monitored by TLC). After the reaction is complete, the solution was concentrated under vacuum and the obtained residue was purified by flash column chromatography on silica gel (petroleum ether and ethyl acetate as eluents, the ratio is 50:1) to afford oxirane **3a** (xxx mg, yield 68%).

### 4.2

Trapping

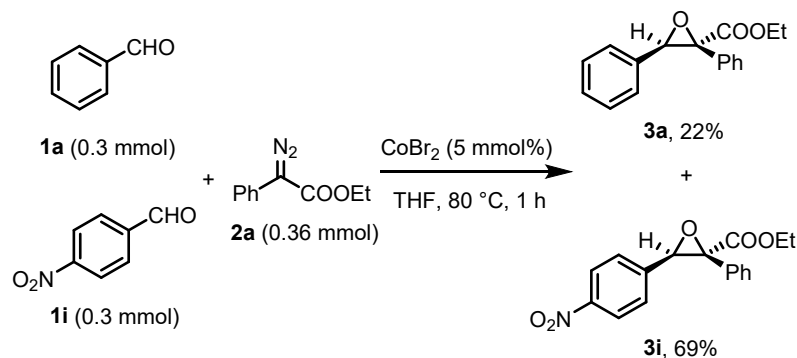


Styrene

Experiment

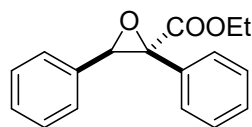
Under Ar atmosphere, to a 10 mL over-dried tube charged with a stir bar and CoBr<sub>2</sub> (5 mol%, 3.3 mg). 1.5 mL THF and styrene (0.3 mmol, 1.0 equiv) was injected into the tube by syringe and stirred for 10 mins in the glovebox, then diazoester **2a** (0.36 mmol, 1.2 equiv) was injected into the tube by syringe. The resultant solution was stirred at 80 °C for 24 hours (monitored by TLC). We didn't obtain desired product **5a** and the almost diazoester **2a** was homocoupling.

### 4.3 Competitive experiments



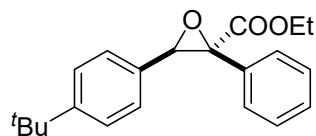
Under Ar atmosphere, to a 10 mL over-dried tube charged with a stir bar and  $\text{CoBr}_2$  (5 mol%, 3.3 mg). 1.5 mL THF. **1a** (0.3 mmol, 1.0 equiv) and **1i** (0.3 mmol, 1.0 equiv) were added and the resulting mixture was stirred for 10 mins in the glovebox, then diazoester **2a** (0.36 mmol, 1.2 equiv) was injected into the tube by syringe. The resultant solution was stirred at 80 °C for 1 hours. the solution was concentrated under vacuum and the obtained residue was purified by flash column chromatography on silica gel (petroleum ether and ethyl acetate as eluents, the ratio is from 50:1 to 10:1) to afford epoxide **3a** (17.6 mg, 22%) and epoxide **3i** (65 mg, 67%).

## 5. Characterization data of oxirane 3a-3ak



### (2*S*,3*R*)-Ethyl-2,3-diphenyloxirane-2-carboxylate (**3a**)

White solid. yield 88% (70.8 mg, 0.3 mmol scale), and purified by flash column chromatography on silica gel (PE/EA = 50/1), **Mp**:52-53 °C;  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  7.29 (m, 2H), 7.21 (m, 3H), 7.13-7.12 (m, 3H), 7.03-7.02 (d,  $J = 6.6$  Hz, 2H), 4.56 (s, 1H), 4.33-4.22 (m, 2H), 1.29 (t,  $J = 7.1$  Hz, 3H);  $^{13}\text{C NMR}$  (100 MHz, Chloroform-*d*)  $\delta$  169.3, 133.1, 131.4, 128.8, 128.2(overlap), 127.8, 127.7, 126.8, 65.1, 63.5, 62.2, 14.1. **HRMS** (EI)  $m/z$ :  $[\text{M}]^+$  Calcd for  $\text{C}_{17}\text{H}_{16}\text{O}_3$  268.1099; Found 268.1093.

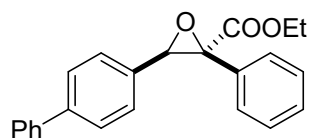


### (2*S*,3*R*)-Ethyl-3-(4-(*tert*-butyl)phenyl)-2-phenyloxirane-2-carboxylate (**3b**)

Colorless oil. yield 93% (91.1 mg, 0.3 mmol scale), and purified by flash column chromatography on silica gel (PE/EA = 10/1);  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  7.32-7.31 (m, 2H), 7.23-7.22 (m, 3H), 7.15 (d,  $J = 8.1$  Hz, 2H), 6.93 (d,  $J = 8.1$  Hz, 2H), 4.52 (s, 1H), 4.29-4.25 (m, 2H), 1.29 (t,  $J = 7.1$  Hz, 3H), 1.22 (s, 9H);  $^{13}\text{C NMR}$  (100 MHz, Chloroform-*d*)  $\delta$  169.5, 151.3, 131.6, 130.0, 128.8, 128.1, 127.7, 126.7, 124.7, 65.2, 63.6, 62.2, 34.5, 31.2, 14.1. **HRMS** (EI)  $m/z$ :  $[\text{M}]^+$  Calcd for  $\text{C}_{21}\text{H}_{24}\text{O}_3$  324.1725;

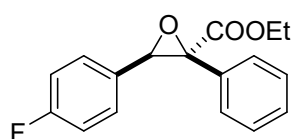


Found 324.1720.



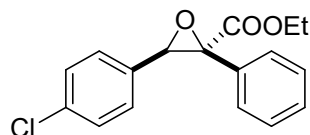
**(2S,3R)-Ethyl-3-([1,1'-biphenyl]-4-yl)-2-phenyloxirane-2-carboxylate (3c)**

White solid. yield 55% (56.8 mg, 0.3 mmol scale), and purified by flash column chromatography on silica gel (PE/EA = 10/1), **Mp**:120-121 °C; **<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.53-7.50 (m, 2H), 7.42-7.31 (m, 7H), 7.27-7.23 (m, 3H), 7.11 (d,  $J = 7.5$  Hz, 2H), 4.62 (s, 1H), 4.35-4.27 (m, 2H), 1.33 (t,  $J = 7.1$  Hz, 3H); **<sup>13</sup>C NMR** (100 MHz, Chloroform-*d*)  $\delta$  169.3, 141.0, 140.4, 132.1 131.4, 128.8, 128.7, 128.3, 127.8, 127.4, 127.3, 127.0, 126.5, 65.3, 63.5, 62.3, 14.1. HRMS (EI)  $m/z$ :  $[M]^+$  Calcd for C<sub>23</sub>H<sub>20</sub>O<sub>3</sub> 344.1412; Found 344.1405.



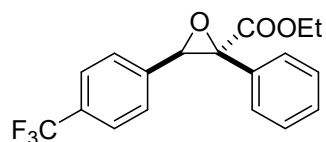
**(2S,3R)-Ethyl-3-(4-fluorophenyl)-2-phenyloxirane-2-carboxylate (3d)**

Colorless oil. yield 80% (68.7 mg, 0.3 mmol scale), and purified by flash column chromatography on silica gel (PE/EA = 50/1); **<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.29-7.26 (m, 2H), 7.23-7.20 (m, 3H), 7.02-6.97 (m, 2H), 6.83-6.79 (m, 2H), 4.54 (s, 1H), 4.30-4.22 (m, 2H), 1.28 (t,  $J = 7.1$  Hz, 3H); **<sup>13</sup>C NMR** (100 MHz, Chloroform-*d*)  $\delta$  169.1, 162.6 (d,  $^1J_{C-F} = 247.2$  Hz), 131.2, 128.9 (d,  $^4J_{C-F} = 3.0$  Hz), 128.7, 128.6 (d,  $^3J_{C-F} = 8.4$  Hz), 128.3, 127.8, 115.0 (d,  $^2J_{C-F} = 21.8$  Hz), 65.1, 62.9, 62.3, 14.1. **<sup>19</sup>F NMR** (376.5 MHz, CDCl<sub>3</sub>)  $\delta$  -113.3. HRMS (EI)  $m/z$ :  $[M]^+$  Calcd for C<sub>17</sub>H<sub>15</sub>FO<sub>3</sub> 286.1005; Found 286.1002.



**(2S,3R)-Ethyl-3-(4-chlorophenyl)-2-phenyloxirane-2-carboxylate (3e)**

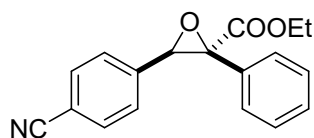
Colorless oil. yield 94% (85.4 mg, 0.3 mmol scale), and purified by flash column chromatography on silica gel (PE/EA = 50/1); **<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.29-7.26 (m, 2H), 7.24-7.20 (m, 3H), 7.11-7.08 (m, 2H), 6.97-6.95 (m, 2H), 4.54 (s, 1H), 4.30-4.22 (m, 2H), 1.28 (t,  $J = 7.1$  Hz, 3H); **<sup>13</sup>C NMR** (100 MHz, Chloroform-*d*)  $\delta$  169.0, 134.2, 131.7, 131.1, 128.7, 128.4, 128.1(overlap), 127.8, 65.2, 62.9, 62.3, 14.1. HRMS (EI)  $m/z$ :  $[M]^+$  Calcd for C<sub>17</sub>H<sub>15</sub>ClO<sub>3</sub> 302.0710; Found 302.0702.



**(2S,3R)-Ethyl-2-phenyl-3-(4-(trifluoromethyl)phenyl)oxirane-2-carboxylate (3f)**

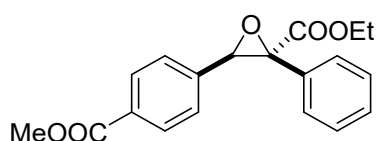
Colorless oil. yield 85% (85.8 mg, 0.3 mmol scale), and purified by flash column chromatography on silica gel (PE/EA = 50/1); **<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.39-7.37 (d,  $J = 8.2$  Hz, 2H), 7.29-7.26 (m, 2H), 7.23-7.20 (m, 3H), 7.17-7.15 (d,  $J = 8.2$  Hz, 2H), 4.62 (s, 1H), 4.31-4.24 (m, 2H), 1.29 (t,  $J = 7.1$  Hz, 3H); **<sup>13</sup>C NMR** (100 MHz, Chloroform-*d*)  $\delta$  168.8, 137.2, 130.8, 130.3 (d,  $^2J_{C-F} = 32.4$  Hz), 128.6, 128.5, 127.9, 127.1, 124.8 (q,  $^1J_{C-F} = 272.3$  Hz), 123.9 (q,  $^3J_{C-F} = 3.8$  Hz), 65.3, 62.7, 62.4, 14.0. **<sup>19</sup>F NMR** (376.5 MHz, CDCl<sub>3</sub>)  $\delta$  -62.7. HRMS (EI)  $m/z$ :  $[M]^+$  Calcd for C<sub>18</sub>H<sub>15</sub>F<sub>3</sub>O<sub>3</sub> 336.0973; Found

336.0967.



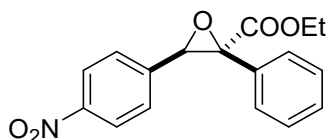
**(2S,3R)-Ethyl-3-(4-cyanophenyl)-2-phenyloxirane-2-carboxylate (3g)**

White solid. yield 94% (85.4 mg, 0.3 mmol scale), and purified by flash column chromatography on silica gel (PE/EA = 50/1), **Mp**:79-80 °C; **<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.42-7.40 (d, *J* = 7.7 Hz, 2H), 7.26-7.22 (m, 5H), 7.16-7.14 (d, *J* = 7.9 Hz, 2H), 4.61 (s, 1H), 4.29-4.24 (m, 2H), 1.28 (t, *J* = 7.1 Hz, 3H); **<sup>13</sup>C NMR** (100 MHz, Chloroform-*d*)  $\delta$  168.5, 138.6, 131.6, 130.6, 128.6, 128.5, 127.9, 127.4, 118.4, 112.1, 65.4, 62.5 (overlap), 14.0. HRMS (EI) *m/z*: [M]<sup>+</sup> Calcd for C<sub>18</sub>H<sub>15</sub>NO<sub>3</sub> 293.1052; Found 293.1051.



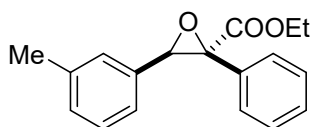
**(2S,3R)-Ethyl-3-(4-(methoxycarbonyl)phenyl)-2-phenyloxirane-2-carboxylate (3h)**

White solid. yield 93% (91.1 mg, 0.3 mmol scale), and purified by flash column chromatography on silica gel (PE/EA = 10/1), **Mp**:88-89 °C; **<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.70-7.78 (d, *J* = 8.4 Hz, 2H), 7.28-7.25 (m, 2H), 7.21-7.18 (m, 3H), 7.15 (d, *J* = 8.3 Hz, 2H), 4.61 (s, 1H), 4.31-4.23 (m, 2H), 3.84 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H); **<sup>13</sup>C NMR** (100 MHz, Chloroform-*d*)  $\delta$  168.9, 166.6, 138.2, 130.9, 129.9, 129.1, 128.6, 128.4, 127.8, 126.7, 65.3, 63.0, 62.4, 52.1, 14.1. HRMS (EI) *m/z*: [M]<sup>+</sup> Calcd for C<sub>19</sub>H<sub>18</sub>O<sub>5</sub> 326.1154; Found 326.1149.



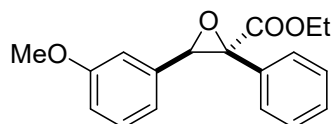
**(2S,3R)-Ethyl-3-(4-nitrophenyl)-2-phenyloxirane-2-carboxylate (3i)**

Yellow solid. yield 91% (85.4 mg, 0.3 mmol scale), and purified by flash column chromatography on silica gel (PE/EA = 10/1), **Mp**:101-102 °C; **<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  8.00-7.98 (d, *J* = 8.2 Hz, 2H), 7.27-7.26 (m, 2H), 7.23-7.21 (m, 5H), 4.66 (s, 1H), 4.31-4.25 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 3H); **<sup>13</sup>C NMR** (100 MHz, Chloroform-*d*)  $\delta$  168.5, 147.7, 140.5, 130.5, 128.7, 128.5, 128.0, 127.6, 123.1, 65.4, 62.6, 62.4, 14.0. HRMS (EI) *m/z*: [M]<sup>+</sup> Calcd for C<sub>17</sub>H<sub>15</sub>NO<sub>5</sub> 313.0950; Found 313.0953.



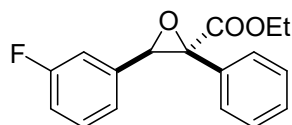
**(2S,3R)-Ethyl-2-phenyl-3-(m-tolyl)oxirane-2-carboxylate (3j)**

Colorless oil. yield 88% (74.5 mg, 0.3 mmol scale), and purified by flash column chromatography on silica gel (PE/EA = 50/1); **<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.30-7.29 (m, 2H), 7.22-7.21 (m, 2H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.95 (d, *J* = 7.4 Hz, 1H), 6.85 (s, 1H), 6.79 (d, *J* = 7.4 Hz, 1H), 4.52 (s, 1H), 4.30-4.23 (m, 2H), 2.18 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H); **<sup>13</sup>C NMR** (100 MHz, Chloroform-*d*)  $\delta$  169.4, 137.4, 133.0, 131.5, 129.0, 128.8, 128.1, 127.7, 127.6(overlap), 123.9, 65.1, 63.6, 62.2, 21.2, 14.1. HRMS (EI) *m/z*: [M]<sup>+</sup> Calcd for C<sub>18</sub>H<sub>18</sub>O<sub>3</sub> 282.1256; Found 282.1256.



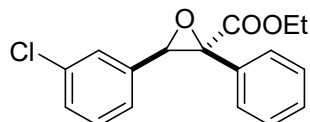
**(2*S*,3*R*)-Ethyl-3-(3-methoxyphenyl)-2-phenyloxirane-2-carboxylate (3k)**

Colorless oil. yield 78% (69.8 mg, 0.3 mmol scale), and purified by flash column chromatography on silica gel (PE/EA = 5/1); **<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.30 (m, 2H), 7.22 (m, 3H), 7.06 (t, *J* = 7.9 Hz, 1H), 6.70 (t, *J* = 9.4 Hz, 2H), 6.43 (s, 1H), 4.53 (s, 1H), 4.28-4.26 (m, 2H), 3.55 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H); **<sup>13</sup>C NMR** (100 MHz, Chloroform-*d*)  $\delta$  169.2, 159.1, 134.6, 131.5, 128.9, 128.8, 128.2, 127.7, 119.5, 114.7, 111.5, 65.1, 63.4, 62.2, 55.0, 14.1. HRMS (EI) *m/z*: [M]<sup>+</sup> Calcd for C<sub>18</sub>H<sub>18</sub>O<sub>4</sub> 298.1205; Found 298.1198.



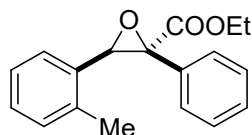
**(2*S*,3*R*)-Ethyl-3-(3-fluorophenyl)-2-phenyloxirane-2-carboxylate (3l)**

colorless oil. yield 89% (76.4 mg, 0.3 mmol scale), and purified by flash column chromatography on silica gel (PE/EA = 50/1); **<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.31-7.28 (m, 2H), 7.23-7.21 (m, 3H), 7.12-7.07 (m, 1H), 6.88-6.80 (m, 2H), 6.73-6.69 (m, 1H), 4.56 (s, 1H), 4.31-4.23 (m, 2H), 1.28 (t, *J* = 7.1 Hz, 3H); **<sup>13</sup>C NMR** (100 MHz, Chloroform-*d*)  $\delta$  168.9, 162.4 (d, <sup>1</sup>*J*<sub>C-F</sub> = 246.2 Hz), 135.9 (d, <sup>3</sup>*J*<sub>C-F</sub> = 7.8 Hz), 131.0, 129.5 (d, <sup>3</sup>*J*<sub>C-F</sub> = 8.4 Hz), 128.6, 128.4, 127.8, 122.5 (d, <sup>4</sup>*J*<sub>C-F</sub> = 2.9 Hz), 115.2 (d, <sup>2</sup>*J*<sub>C-F</sub> = 21.2 Hz), 113.8 (d, <sup>2</sup>*J*<sub>C-F</sub> = 23.2 Hz), 65.2, 62.8 (d, <sup>4</sup>*J*<sub>C-F</sub> = 2.4 Hz), 62.3, 14.1. **<sup>19</sup>F NMR** (376.5 MHz, CDCl<sub>3</sub>)  $\delta$  -113.1. HRMS (EI) *m/z*: [M]<sup>+</sup> Calcd for C<sub>17</sub>H<sub>15</sub>FO<sub>3</sub> 286.1005; Found 286.1000.



**(2*S*,3*R*)-Ethyl-3-(3-chlorophenyl)-2-phenyloxirane-2-carboxylate (3m)**

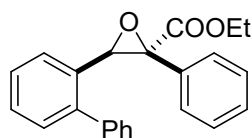
Colorless oil. yield 84% (77.2 mg, 0.3 mmol scale), and purified by flash column chromatography on silica gel (PE/EA = 50/1); **<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.30-7.28 (m, 2H), 7.23-7.22 (m, 3H), 7.12-7.10 (m, 1H), 7.04 (t, *J* = 7.8 Hz, 2H), 6.89 (d, *J* = 7.8 Hz, 1H), 4.53 (s, 1H), 4.31-4.23 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 3H); **<sup>13</sup>C NMR** (100 MHz, Chloroform-*d*)  $\delta$  168.9, 135.3, 133.9, 130.1, 129.1, 128.7, 128.4, 127.8, 127.0, 124.9, 65.1, 62.7, 62.4, 14.1. HRMS (EI) *m/z*: [M]<sup>+</sup> Calcd for C<sub>17</sub>H<sub>15</sub>ClO<sub>3</sub> 302.0710; Found 302.0712.



**(2*S*,3*R*)-Ethyl-2-phenyl-3-(o-tolyl)oxirane-2-carboxylate (3n)**

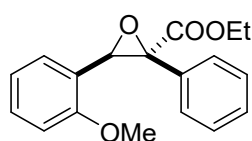
White solid. yield 69% (58.4 mg, 0.3 mmol scale), and purified by flash column chromatography on silica gel (PE/EA = 50/1), **Mp**: 34-35 °C; **<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.33-7.31 (m, 2H), 7.16-7.15 (m, 3H), 7.05-7.00 (m, 2H), 6.97 (d, *J* = 7.5 Hz, 1H), 6.91 (t, *J* = 7.0 Hz, 1H), 4.61 (s, 1H), 4.35-4.27 (m, 2H), 2.38 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H); **<sup>13</sup>C NMR** (100 MHz, Chloroform-*d*)  $\delta$  169.3, 135.5, 131.4, 131.3, 129.4, 128.1, 128.0, 127.8, 127.5, 126.2, 125.3, 64.6, 62.8, 62.2, 18.8, 14.1. **HRMS** (EI)

m/z: [M]<sup>+</sup> Calcd for C<sub>18</sub>H<sub>18</sub>O<sub>3</sub> 282.1256; Found 282.1251.



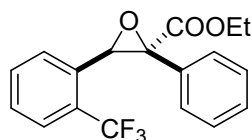
**(2S,3R)-Ethyl-3-([1,1'-biphenyl]-2-yl)-2-phenyloxirane-2-carboxylate (3o)**

White solid. yield 83% (85.6 mg, 0.3 mmol scale), and purified by flash column chromatography on silica gel (PE/EA = 50/1), **Mp**:86-87 °C; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.52-7.45 (m, 7H), 7.26 (m, 5H), 7.11-7.07 (m, 1H), 7.01 (d, *J* = 7.5 Hz, 1H), 4.48 (s, 1H), 4.30-4.17 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H); <sup>13</sup>C NMR (100 MHz, Chloroform-*d*) δ 168.9, 141.5, 139.8, 131.2, 130.2, 129.3, 129.2, 128.7, 128.4, 128.3, 128.1, 127.7, 127.6, 126.7, 126.6, 65.5, 63.2, 62.0, 14.2. HRMS (EI) m/z: [M]<sup>+</sup> Calcd for C<sub>23</sub>H<sub>20</sub>O<sub>3</sub> 344.1412; Found 344.1407.



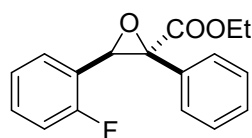
**(2S,3R)-Ethyl-3-(2-methoxyphenyl)-2-phenyloxirane-2-carboxylate (3p)**

Colorless oil. yield 70% (62.7 mg, 0.3 mmol scale), and purified by flash column chromatography on silica gel (PE/EA = 5/1); <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.33-7.31 (m, 2H), 7.16-7.14 (m, 3H), 7.11-7.07 (m, 1H), 6.84 (dd, *J* = 1.5 Hz, 1H), 6.74 (d, *J* = 8.2 Hz, 1H), 6.64 (t, *J* = 7.5 Hz, 1H), 4.74 (s, 1H), 4.33-4.26 (m, 2H), 3.86 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H); <sup>13</sup>C NMR (100 MHz, Chloroform-*d*) δ 169.6, 157.7, 131.9, 129.0, 128.4, 127.9, 127.4, 127.3, 121.9, 119.8, 109.6, 64.4, 62.1, 60.7, 55.4, 14.1. HRMS (EI) m/z: [M]<sup>+</sup> Calcd for C<sub>18</sub>H<sub>18</sub>O<sub>4</sub> 298.1205; Found 298.1202.



**(2S,3R)-Ethyl-2-phenyl-3-(2-(trifluoromethyl)phenyl)oxirane-2-carboxylate (3q)**

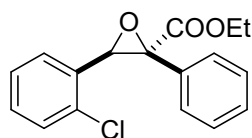
Colorless oil. yield 74% (74.7 mg, 0.3 mmol scale), and purified by flash column chromatography on silica gel (PE/EA = 50/1); <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.54-7.52 (m, 1H), 7.34-7.32 (m, 2H), 7.24-7.22 (m, 2H), 7.16-7.14 (m, 4H), 4.87 (d, *J* = 1.5 Hz, 1H), 4.38-4.23 (m, 2H), 1.31 (t, *J* = 7.1 Hz, 3H); <sup>13</sup>C NMR (100 MHz, Chloroform-*d*) δ 168.5, 131.5, 131.2, 130.8, 128.5, 128.2, 128.0, 125.9, 125.4 (q, <sup>4</sup>*J*<sub>C-F</sub> = 1.5 Hz), 124.3 (q, <sup>1</sup>*J*<sub>C-F</sub> = 273.6 Hz), 65.1, 62.3, 61.1 (<sup>4</sup>*J*<sub>C-F</sub>, *J* = 3.0 Hz), 14.0. <sup>19</sup>F NMR (376.5 MHz, CDCl<sub>3</sub>) δ -60.0. HRMS (EI) m/z: [M]<sup>+</sup> Calcd for C<sub>18</sub>H<sub>15</sub>F<sub>3</sub>O<sub>3</sub> 336.0973; Found 336.0964.



**(2S,3R)-Ethyl-3-(2-fluorophenyl)-2-phenyloxirane-2-carboxylate (3r)**

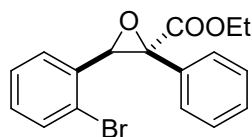
White solid. yield 80% (68.7 mg, 0.3 mmol scale), and purified by flash column chromatography on silica gel (PE/EA = 50/1), **Mp**:59-60 °C; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.34-7.31 (m, 2H), 7.22-7.16 (m, 3H), 7.14-7.08 (m, 1H), 6.96-6.91 (t, *J* = 9.3 Hz, 1H), 6.85-6.78 (m, 2H), 4.76 (s, 1H), 4.35-4.23 (m, 2H), 1.30 (t, *J* = 7.1 Hz, 3H); <sup>13</sup>C NMR (100 MHz, Chloroform-*d*) δ 168.9, 161.2 (d, <sup>1</sup>*J*<sub>C-F</sub> = 246.7 Hz), 131.3, 129.6 (d, <sup>3</sup>*J*<sub>C-F</sub> = 8.1 Hz), 128.4, 128.2, 128.0 (d, <sup>4</sup>*J*<sub>C-F</sub> = 3.4 Hz), 127.7, 123.5 (d, <sup>3</sup>*J*<sub>C-F</sub>

= 3.5 Hz), 121.0 (d,  $^2J_{C-F}$  = 12.8 Hz), 114.6 (d,  $^2J_{C-F}$  = 20.2 Hz), 64.6, 62.3, 59.0 (d,  $^3J_{C-F}$  = 6.0 Hz), 14.1.  $^{19}\text{F}$  NMR (376.5 MHz,  $\text{CDCl}_3$ )  $\delta$  -119.3. HRMS (EI) m/z:  $[\text{M}]^+$  Calcd for  $\text{C}_{17}\text{H}_{15}\text{FO}_3$  286.1005; Found 286.1002.



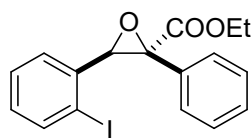
**(2S,3R)-Ethyl-3-(2-chlorophenyl)-2-phenyloxirane-2-carboxylate (3s)**

White solid. yield 92% (83.6 mg, 0.3 mmol scale), and purified by flash column chromatography on silica gel (PE/EA = 50/1), **Mp**:69-70 °C;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.36-7.34 (m, 2H), 7.23-7.21 (m, 1H), 7.16-7.15 (m, 3H), 7.09-7.04 (m, 1H), 7.00-6.95 (m, 2H), 4.76 (s, 1H), 4.35-4.26 (m, 2H), 1.32 (t,  $J$  = 7.1 Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  168.9, 132.8, 131.5, 131.2, 129.2, 128.7, 128.2(overlap), 127.9, 127.5, 126.2, 64.5, 62.3, 62.0, 14.1. HRMS (EI) m/z:  $[\text{M}]^+$  Calcd for  $\text{C}_{17}\text{H}_{15}\text{ClO}_3$  302.0710; Found 302.0705.



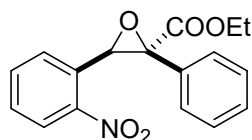
**(2S,3R)-Ethyl-3-(2-bromophenyl)-2-phenyloxirane-2-carboxylate (3t)**

White solid. yield 85% (88.5 mg, 0.3 mmol scale), and purified by flash column chromatography on silica gel (PE/EA = 50/1), **Mp**:80-81 °C;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.40-7.36 (m, 3H), 7.16-7.14 (m, 3H), 7.04-6.97 (m, 3H), 4.70 (s, 1H), 4.36-4.26 (m, 2H), 1.32 (t,  $J$  = 7.1 Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  168.8, 133.0, 131.8, 131.1, 129.4, 128.3, 128.2, 128.1, 127.5, 126.7, 122.2, 64.4, 64.0, 62.3, 14.1. HRMS (EI) m/z:  $[\text{M}]^+$  Calcd for  $\text{C}_{17}\text{H}_{15}\text{BrO}_3$  346.0205; Found 346.0197.



**(2S,3R)-Ethyl-3-(2-iodophenyl)-2-phenyloxirane-2-carboxylate (3u)**

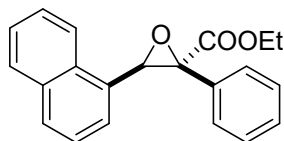
White solid. yield 92% (108.8 mg, 0.3 mmol scale), and purified by flash column chromatography on silica gel (PE/EA = 50/1), **Mp**:87-88 °C;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.66-7.64 (d,  $J$  = 7.8 Hz, 1H), 7.41-7.40 (m, 2H), 7.16-7.15 (m, 3H), 7.06 (t,  $J$  = 7.5 Hz, 1H), 6.95 (d,  $J$  = 7.6 Hz, 1H), 6.84 (t,  $J$  = 7.5 Hz, 1H), 4.58 (s, 1H), 4.38-4.28 (m, 2H), 1.33 (t,  $J$  = 7.1 Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  168.8, 138.2, 135.8, 131.0, 129.6, 128.4, 128.1, 127.5, 96.2, 68.0, 64.5, 62.3, 14.2. HRMS (EI) m/z:  $[\text{M}]^+$  Calcd for  $\text{C}_{17}\text{H}_{15}\text{IO}_3$  394.0066; Found 394.0059.



**(2S,3R)-Ethyl-3-(2-nitrophenyl)-2-phenyloxirane-2-carboxylate (3v)**

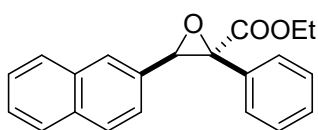
Yellow solid. yield 50% (47.0 mg, 0.3 mmol scale), and purified by flash column chromatography on silica gel (PE/EA = 5/1), **Mp**:94-95 °C;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.04-8.02 (m, 1H), 7.44-7.40 (m, 2H), 7.33-7.29 (m, 3H), 7.12-7.11 (m, 3H), 5.10 (s, 1H), 4.42-4.27 (m, 2H), 1.34 (t,  $J$  = 7.1 Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  168.4, 147.0, 133.7, 131.1, 130.6, 129.2, 128.9, 128.2, 127.9,

127.6, 124.4, 64.4, 63.0, 62.5, 14.1. HRMS (EI)  $m/z$ :  $[M]^+$  Calcd for  $C_{17}H_{15}NO_5$  313.0950; Found 313.0950.



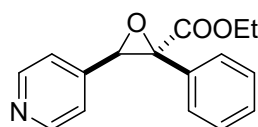
**(2*S*,3*R*)-Ethyl-3-(naphthalen-1-yl)-2-phenyloxirane-2-carboxylate (3w)**

Colorless oil. yield 91% (86.9 mg, 0.3 mmol scale), and purified by flash column chromatography on silica gel (PE/EA = 10/1);  $^1H$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.09 (d,  $J$  = 8.4 Hz, 1H), 7.79 (d,  $J$  = 8.2 Hz, 1H), 7.62-7.57 (m, 2H), 7.49 (t,  $J$  = 7.5 Hz, 1H), 7.30-7.28 (m, 2H), 7.23-7.19 (m, 2H), 7.05-7.03 (m, 3H), 5.12 (s, 1H), 4.44-4.32 (m, 2H), 1.37 (t,  $J$  = 7.1 Hz, 3H);  $^{13}C$  NMR (100 MHz, Chloroform-*d*)  $\delta$  169.4, 132.9, 131.3, 130.8, 128.8, 128.3, 128.0, 127.9, 127.4, 126.5, 125.8, 124.9, 124.3, 122.6, 65.2, 62.6, 62.3, 14.2. HRMS (EI)  $m/z$ :  $[M]^+$  Calcd for  $C_{21}H_{18}O_3$  318.1256; Found 318.1251.



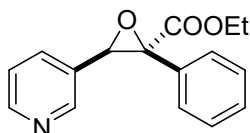
**(2*S*,3*R*)-Ethyl-3-(naphthalen-2-yl)-2-phenyloxirane-2-carboxylate (3x)**

Colorless oil. yield 97% (92.6 mg, 0.3 mmol scale), and purified by flash column chromatography on silica gel (PE/EA = 10/1);  $^1H$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.72-7.67 (m, 2H), 7.58(d,  $J$  = 9.4 Hz, 2H), 7.42-7.40 (m, 2H), 7.34-7.32 (m, 2H), 7.18-7.17 (m, 3H), 7.05 (d,  $J$  = 8.5 Hz, 1H), 4.72 (s, 1H), 4.32-4.27 (m, 2H), 1.31 (t,  $J$  = 7.2 Hz, 3H);  $^{13}C$  NMR (100 MHz, Chloroform-*d*)  $\delta$  169.3, 133.1, 132.7, 131.4, 130.7, 128.8, 128.2, 127.9, 127.7, 127.5, 126.7, 126.2, 124.0, 65.4, 63.8, 62.3, 14.1. HRMS (EI)  $m/z$ :  $[M]^+$  Calcd for  $C_{21}H_{18}O_3$  318.1256; Found 318.1253.



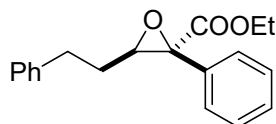
**(2*S*,3*R*)-Ethyl-2-phenyl-3-(pyridin-4-yl)oxirane-2-carboxylate (3y)**

Brown oil. yield 69% (55.7 mg, 0.3 mmol scale), and purified by flash column chromatography on silica gel (PE/EA = 10/1);  $^1H$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.35 (d,  $J$  = 4.5 Hz, 2H), 7.26-7.24 (m, 2H), 7.20 (m, 3H), 6.95 (d,  $J$  = 4.7 Hz, 2H), 4.53 (s, 1H), 4.28-4.23 (m, 2H), 1.27 (t,  $J$  = 7.1 Hz, 3H);  $^{13}C$  NMR (100 MHz, Chloroform-*d*)  $\delta$  168.5, 149.3, 142.3, 130.5, 128.6, 128.5, 127.9, 121.6, 65.2, 62.5, 61.9, 14.0. HRMS (EI)  $m/z$ :  $[M]^+$  Calcd for  $C_{16}H_{15}NO_3$  269.1052; Found 269.1045.



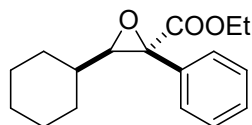
**(2*S*,3*R*)-Ethyl-2-phenyl-3-(pyridin-3-yl)oxirane-2-carboxylate (3z)**

Brown oil. yield 75% (60.6 mg, 0.3 mmol scale), and purified by flash column chromatography on silica gel (PE/EA = 10/1);  $^1H$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.42-8.38 (m, 2H), 7.30-7.28 (m, 2H), 7.22-7.17 (m, 4H), 7.01-6.98 (m, 1H), 4.60 (s, 1H), 4.30-4.22 (m, 2H), 1.28 (t,  $J$  = 7.1 Hz, 3H);  $^{13}C$  NMR (100 MHz, Chloroform-*d*)  $\delta$  168.7, 149.5, 148.5, 134.1, 130.7, 129.2, 128.6, 128.5, 127.9, 122.7, 65.2, 62.4, 61.4, 14.0. HRMS (EI)  $m/z$ :  $[M]^+$  Calcd for  $C_{16}H_{15}NO_3$  269.1052; Found 269.1041.



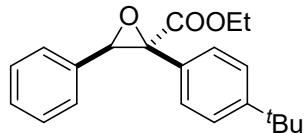
**(2*S*,3*R*)-Ethyl-3-phenethyl-2-phenyloxirane-2-carboxylate (3aa)**

Colorless oil. yield 70% (62.2 mg, 0.3 mmol scale), and purified by flash column chromatography on silica gel (PE/EA = 50/1); <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.46-7.44 (m, 2H), 7.39-7.34 (m, 3H), 7.26-7.23 (m, 2H), 7.18 (t, *J* = 7.1 Hz, 1H), 7.07 (d, *J* = 7.2 Hz, 1H), 4.29-4.17 (m, 2H), 3.55 (t, *J* = 6.0 Hz, 1H), 2.79-2.66 (m, 2H), 1.62-1.46 (m, 2H), 1.27 (t, *J* = 7.1 Hz, 3H); <sup>13</sup>C NMR (100 MHz, Chloroform-*d*)  $\delta$  169.6, 140.7, 132.5, 128.5, 128.4, 128.3, 128.0(overlap), 126.1, 63.2, 62.7, 62.0, 32.1, 30.2, 14.1. HRMS (EI) *m/z*: [M]<sup>+</sup> Calcd for C<sub>19</sub>H<sub>20</sub>O<sub>3</sub> 296.1412; Found 296.1410.



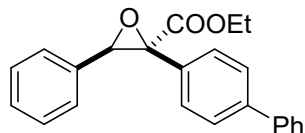
**(2*S*,3*R*)-Ethyl-3-cyclohexyl-2-phenyloxirane-2-carboxylate (3ab)**

Colorless oil. yield 82% (67.5 mg, 0.3 mmol scale), and purified by flash column chromatography on silica gel (PE/EA = 10/1); <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.51-7.49 (m, 2H), 7.38-7.30 (m, 3H), 4.27-4.15 (m, 2H), 3.18 (d, *J* = 9.2 Hz, 1H), 1.86-1.83 (m, 1H), 1.68-1.65 (m, 1H), 1.60-1.51 (m, 3H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.22-0.98 (m, 4H), 0.96-0.86 (m, 1H), 0.73-0.63 (m, 1H); <sup>13</sup>C NMR (100 MHz, Chloroform-*d*)  $\delta$  169.9, 132.8, 128.1, 127.9, 127.8, 67.9, 62.7, 61.9, 36.4, 30.0, 27.9, 26.0, 25.1, 25.0, 14.0. HRMS (EI) *m/z*: [M]<sup>+</sup> Calcd for C<sub>17</sub>H<sub>22</sub>O<sub>3</sub> 274.1569; Found 274.1568.



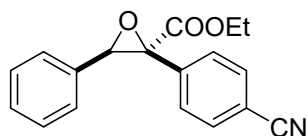
**(2*S*,3*R*)-Ethyl-2-(4-(tert-butyl)phenyl)-3-phenyloxirane-2-carboxylate (3ac)**

Colorless oil. yield 90% (87.6 mg, 0.3 mmol scale), and purified by flash column chromatography on silica gel (PE/EA = 10/1); <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.23(s, 4H), 7.16-7.09 (m, 3H), 7.03-7.01 (m, 2H), 4.53 (s, 1H), 4.33-4.21 (m, 2H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.25 (s, 9H); <sup>13</sup>C NMR (100 MHz, Chloroform-*d*)  $\delta$  169.5, 151.1, 133.2, 128.4, 128.3, 128.1, 127.7, 126.9, 124.6, 65.2, 63.5, 62.1, 34.5, 31.2, 14.1. HRMS (EI) *m/z*: [M]<sup>+</sup> Calcd for C<sub>21</sub>H<sub>24</sub>O<sub>3</sub> 324.1725; Found 324.1724.



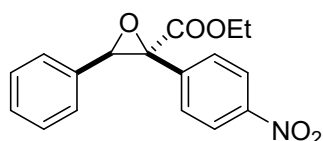
**(2*S*,3*R*)-Ethyl-2-([1,1'-biphenyl]-4-yl)-3-phenyloxirane-2-carboxylate (3ad)**

White solid. yield 83% (87.8 mg, 0.3 mmol scale), and purified by flash column chromatography on silica gel (PE/EA = 10/1), **Mp**: 97-98 °C; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.55 (d, *J* = 7.4 Hz, 2H), 7.47 (d, *J* = 8.3 Hz, 2H), 7.43-7.38 (m, 4H), 7.33 (t, *J* = 7.3 Hz, 1H), 7.17-7.15 (m, 3H), 7.10-7.08 (m, 2H), 4.61 (s, 1H), 4.35-4.27 (m, 2H), 1.33 (t, *J* = 7.1 Hz, 3H); <sup>13</sup>C NMR (100 MHz, Chloroform-*d*)  $\delta$  169.3, 140.9, 140.5, 133.1, 130.4, 129.2, 128.8, 128.3, 127.9, 127.4, 127.0, 126.9, 126.4, 65.1, 63.7, 62.3, 14.1. HRMS (EI) *m/z*: [M]<sup>+</sup> Calcd for C<sub>23</sub>H<sub>20</sub>O<sub>3</sub> 344.1412; Found 344.1413.



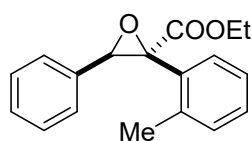
**(2*S*,3*R*)-Ethyl-2-(4-cyanophenyl)-3-phenyloxirane-2-carboxylate (3ae)**

White solid. yield 41% (36.1 mg, 0.3 mmol scale), and purified by flash column chromatography on silica gel (PE/EA = 50/1), **Mp**:95-96 °C; **<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.51-7.49 (m, 2H), 7.43-7.41 (m, 2H), 7.18-7.12 (m, 3H), 7.01-6.99 (m, 2H), 4.64 (s, 1H), 4.32-4.26 (m, 2H), 1.30 (t,  $J$  = 7.1 Hz, 3H); **<sup>13</sup>C NMR** (100 MHz, Chloroform-*d*)  $\delta$  168.2, 136.8, 132.2, 131.5, 129.6, 128.6, 128.1, 126.5, 118.4, 112.2, 64.5, 63.8, 62.7, 14.1. HRMS (EI)  $m/z$ : [M]<sup>+</sup> Calcd for C<sub>18</sub>H<sub>15</sub>NO<sub>3</sub> 293.1052; Found 293.1041.



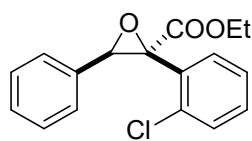
**(2*S*,3*R*)-Ethyl-2-(4-nitrophenyl)-3-phenyloxirane-2-carboxylate (3af)**

Yellow solid. yield 42% (39.5 mg, 0.3 mmol scale), and purified by flash column chromatography on silica gel (PE/EA = 10/1), **Mp**:75-76 °C; **<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  8.08 (d,  $J$  = 8.8 Hz, 2H), 7.49 (d,  $J$  = 8.8 Hz, 2H), 7.17-7.12 (m, 3H), 7.04-7.01 (m, 2H), 4.66 (s, 1H), 4.31 (q,  $J$  = 7.1 Hz, 2H), 1.31 (t,  $J$  = 7.1 Hz, 3H); **<sup>13</sup>C NMR** (100 MHz, Chloroform-*d*)  $\delta$  168.1, 147.6, 138.8, 132.1, 129.8, 128.7, 128.2, 126.4, 122.9, 64.4, 63.9, 62.8, 14.1. HRMS (EI)  $m/z$ : [M]<sup>+</sup> Calcd for C<sub>17</sub>H<sub>15</sub>NO<sub>5</sub> 313.0950; Found 313.0939.



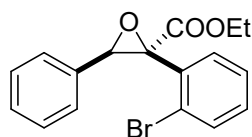
**(2*S*,3*R*)-Ethyl-3-phenyl-2-(o-tolyl)oxirane-2-carboxylate (3ag)**

Colorless oil. yield 59% (50.0 mg, 0.3 mmol scale), and purified by flash column chromatography on silica gel (PE/EA = 50/1); **<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.19-7.09 (m, 6H), 6.98 (d,  $J$  = 7.2 Hz, 3H), 4.64 (s, 1H), 4.33-4.19 (m, 2H), 2.06 (br, 1H), 1.27 (t,  $J$  = 7.1 Hz, 3H); **<sup>13</sup>C NMR** (100 MHz, Chloroform-*d*)  $\delta$  169.3, 133.2, 130.4, 129.8, 129.4, 128.4, 127.7, 127.0, 125.2, 64.9, 63.7, 62.2, 19.1, 14.1. HRMS (EI)  $m/z$ : [M]<sup>+</sup> Calcd for C<sub>18</sub>H<sub>18</sub>O<sub>3</sub> 282.1256; Found 282.1254.



**(2*S*,3*R*)-Ethyl-2-(2-chlorophenyl)-3-phenyloxirane-2-carboxylate (3ah)**

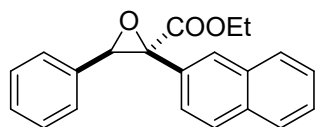
Colorless oil. yield 80% (72.7 mg, 0.3 mmol scale), and purified by flash column chromatography on silica gel (PE/EA = 50/1); **<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.49 (m, 1H), 7.23-7.09 (m, 6H), 7.07-7.05 (m, 2H), 4.84 (s, 1H), 4.36-4.19 (m, 2H), 1.27 (t,  $J$  = 7.1 Hz, 3H); **<sup>13</sup>C NMR** (100 MHz, Chloroform-*d*)  $\delta$  168.2, 132.6, 130.8, 130.5, 129.6, 128.9, 128.3, 127.6, 126.9, 126.1, 64.4, 63.8, 62.4, 14.0. HRMS (EI)  $m/z$ : [M]<sup>+</sup> Calcd for C<sub>17</sub>H<sub>15</sub>ClO<sub>3</sub> 302.0710; Found 302.0706.





**(2*S*,3*R*)-Ethyl-2-(2-bromophenyl)-3-phenyloxirane-2-carboxylate (3ai)**

White solid. yield 59% (61.5 mg, 0.3 mmol scale), and purified by flash column chromatography on silica gel (PE/EA = 50/1), **Mp**:79-80 °C; **<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.49 (m, 1H), 7.23-7.09 (m, 6H), 7.07-7.05 (m, 2H), 4.84 (s, 1H), 4.36-4.19 (m, 2H), 1.27 (t, *J* = 7.1 Hz, 3H); **<sup>13</sup>C NMR** (100 MHz, Chloroform-*d*)  $\delta$  168.2, 132.6, 130.8, 130.5, 129.6, 128.9, 128.3, 127.6, 126.9, 126.1, 64.3, 63.8, 62.4, 14.0. HRMS (EI) *m/z*: [M]<sup>+</sup> Calcd for C<sub>17</sub>H<sub>15</sub>BrO<sub>3</sub> 346.0205; Found 346.0196.



**(2*S*,3*R*)-Ethyl-2-(naphthalen-2-yl)-3-phenyloxirane-2-carboxylate (3aj)**

Colorless oil. yield 72% (68.8 mg, 0.3 mmol scale), and purified by flash column chromatography on silica gel (PE/EA = 10/1); **<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.89 (s, 1H), 7.81-7.77 (m, 2H), 7.70 (d, *J* = 8.5 Hz, 1H), 7.49-7.45 (m, 2H), 7.39 (dd, *J* = 8.5 Hz, 1.5 Hz, 1H), 7.11 (s, 5H), 4.69 (s, 1H), 4.37-4.26 (m, 2H), 1.32 (t, *J* = 7.1 Hz, 3H); **<sup>13</sup>C NMR** (100 MHz, Chloroform-*d*)  $\delta$  169.3, 133.0, 132.6, 129.1, 128.3, 128.2, 128.1, 127.9, 127.7, 127.4, 126.8, 126.3, 126.1, 65.4, 63.8, 62.3, 14.1. HRMS (EI) *m/z*: [M]<sup>+</sup> Calcd for C<sub>21</sub>H<sub>18</sub>O<sub>3</sub> 318.1256; Found 318.1254.

## 6. References

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2. Guptill, D. M.; Cohen, C. M.; Davies, H. M. L. Rhodium(II)-Catalyzed Stereoselective Synthesis of Allylsilanes. *Org. Lett.* **2013**, *15*, 6120-6123.
3. Hari, D. P.; Waser, J. Copper-Catalyzed Oxy-Alkynylation of Diazo Compounds with Hypervalent Iodine Reagents. *J. Am. Chem. Soc.* **2016**, *138*, 2190-2193.

