# Electronic Supplementary Information

# Direct annulation between glycine derivatives and thiiranes through photoredox/iron cooperative catalysis

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## **1. Experiment Information**

#### **1.1 General information**

Unless otherwise noted, all reagents were purchased from commercial sources and used as received without further purification. *N*-arylglycine derivatives<sup>1</sup> and thiirane derivatives<sup>2</sup> were prepared according to literature procedures. Unless otherwise indicated, all experiments were carried out under air atmosphere. Irradiation of photochemical reactions was carried out using 18 W blue LED bulb or 5 W LED waveband light source. The LED bulb was purchased from Taobao store (Tai Di lighting, model number: YFGS-9). The silica gel (200–300 meshes) was used for column chromatography and TLC inspections were taken on silica gel GF254 plates. Liquid <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometer. High resolution mass spectra (HRMS) were obtained on a mass spectrometer by using electrospray ionization (ESI) analyzed by quadrupole time-of-flight (QTof).

# **1.2** General procedure for the visible-light-induced aerobic oxidative [2 + 3] cycloaddition between glycine derivatives and thiiranes.

To a solution of *N*-arylglycine derivative (0.2 mmol, 1 eq) and Rh-6G (2 mol%) in dry DCE/CH<sub>3</sub>CN (25/1, 2 mL) was added FeSO<sub>4</sub>·7H<sub>2</sub>O (20 mol%). The mixed solution was irradiated with 18 W blue LEDs under air atmosphere at room temperature, until the glycine derivatives were gone (monitored by TLC), then **2** (0.15 mmol, 1.5 eq) and HI (0.03 mmol, 15 mol%) were added and stirred at room temperature (without the irradiation of blue LEDs). After completion of the reaction as monitored by TLC, the solvent was removed under vacuo, and the residue was purified by silica gel column chromatography (with PE/EA = 64/1 to 16/1 as eluent) to afford the products.

# **1.3** General procedure for the visible-light-induced aerobic oxidative [2 + 3] cycloaddition between glycine derived peptides and thiiranes.

To a solution of glycine derived peptide (0.2 mmol, 1 eq) and Rh-6G (2 mol%) in dry DCE/CH<sub>3</sub>CN (25/1, 2 mL) was added FeSO<sub>4</sub>·7H<sub>2</sub>O (20 mol%). The mixed solution was irradiated with 18 W blue LEDs under O<sub>2</sub> atmosphere at room temperature, until the glycine dipeptides were gone (monitored by TLC), then **2** (0.15 mmol, 1.5 eq) and HI (0.12 mmol, 30 mol%) were added and stirred at room temperature (without the irradiation of blue LEDs). After completion of the reaction as monitored by TLC, the

solvent was removed under vacuo, and the residue was purified by silica gel column chromatography (with PE/EA = 32/1 to 8/1 as eluent) to afford the products. *Note: The reaction can also be carried out under air atmosphere, but the reaction rate is slow.* 



Fig. S1 Picture of photoreaction device.

#### 1.4 Gram Scale Experiment



To a solution of **1a** (5 mmol, 1.05 g, 1 eq) and Rh-6G (0.1 mmol, 48 mg, 2 mol%) in dry DCE/CH<sub>3</sub>CN (25/1, 50 mL) was added FeSO<sub>4</sub>·7H<sub>2</sub>O (1 mmol, 278 mg, 20 mol%). The mixed solution was irradiated with 18 W blue LEDs under air atmosphere at room temperature for 24 h, then **2a** (7.5 mmol, 1.02 g, 1.5 eq) and HI (0.75 mmol, 15 mol%) were added and stirred for another 6 h at room temperature (without the irradiation of blue LEDs). After completion of the reaction as monitored by TLC, the solvent was removed under vacuo, and the residue was purified by silica gel column chromatography (with PE/EA = 64/1 to 16/1 as eluent) to afford **3a** (yellow oil, 78 % yield, > 20:1 dr).



To a solution of 1x (5 mmol, 1.05 g, 1 eq) and Rh-6G (0.1 mmol, 48 mg, 2 mol%) in dry DCE/CH<sub>3</sub>CN (25/1, 50 mL) was added FeSO<sub>4</sub>·7H<sub>2</sub>O (1 mmol, 278 mg, 20 mol%).

The mixed solution was irradiated with 18 W blue LEDs under air atmosphere at room temperature for 36 h, then **2a** (7.5 mmol, 1.02 g, 1.5 eq) and HI (1.5 mmol, 30 mol%) was added and stirred at room temperature for another 15 h (without the irradiation of blue LEDs). After completion of the reaction as monitored by TLC, the solvent was removed under vacuo, and the residue was purified by silica gel column chromatography (with PE/EA = 32/1 to 8/1 as eluent) to afford **4a** (white solid, 58 % yield, > 20:1 dr).



Fig. S2 Picture of set-up for the gram scale reaction.

#### 1.5 Synthesis of compound 8a



3a (0.2 mmol, 68.6 mg) was dissolved in DCM (4 mL), then *m*-CPBA (0.4 mmol, 70 mg) was added and stirred at room temperature. After completion of the reaction as monitored by TLC, the solvent was removed under vacuo, and the residue was purified by silica gel column chromatography to afford **8a**.

1.6 Synthesis of compound 8b



To the suspension of LiAlH<sub>4</sub> (0.12 g, 3.2 mmol) in dry ether (25 mL) was added the solution of **3a** (1.1 g, 3.2 mmol) in dry ether (25 mL) over a period of 10 minutes at 0  $^{\circ}$ C and let stir at the same temperature for another 1 h. The reaction mixture was then diluted with ether (50 mL) and small ice pieces were added carefully. The solid formed was filtered and the filtrate was evaporated to afford **8b** as a colorless liquid, which was taken ahead to the next step without further purification.

#### 1.7 Synthesis of compound 8c



**8b** (0.2 mmol, 60.2 mg) was dissolved in DCM (4 mL) and placed in an ice bath, then  $Et_3N$  (0.3 mmol, 30.4 mg), DMAP (0.3 mmol, 37 mg), EDCI (0.4 mmol, 79.6 mg) and 4-(bis(2-chloroethyl)amino)benzoic acid (0.4 mmol, 104.4 mg) were added respectively. The mixture was stirred at 0 °C for 30 min and then allowed to react at room temperature. After completion of the reaction as monitored by TLC, the reaction was quenched by adding water, and then extracted with DCM and dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under vacuo, and the residue was purified by silica gel column chromatography to afford **8c**.

#### 1.8 Synthesis of compound 8d



**8b** (0.2 mmol, 60.2 mg) was dissolved in DCM (4 mL) and placed in an ice bath, then  $Et_3N$  (0.3 mmol, 30.4 mg), DMAP (0.3 mmol, 37 mg), EDCI (0.4 mmol, 79.6 mg) and Cbz-Glu-Bn (0.4 mmol, 104.4 mg) were added respectively. The mixture was stirred at 0 ° C for 30 min and then allowed to react at room temperature. After completion of the reaction as monitored by TLC, the reaction was quenched by adding water, and then extracted with DCM and dried with anhydrous  $Na_2SO_4$ . The solvent was removed under vacuo, and the residue was purified by silica gel column chromatography to afford **8d**.

## 1.9 Substrate limitation



Scheme S1 Unsuccessful glycine derivatives and thiiranes (NR means no reaction).

### 1.10 Gram-scale reaction and synthetic application of the product





Scheme S2 Gram-scale reaction and synthetic application of the product.

## 2. Optimization of Reaction Conditions

MeO	$N \rightarrow OEt + S$ $H \rightarrow OEt + 2a$	FeSO <sub>4</sub> •7H <sub>2</sub> O, HI, Rh-6G light, DCE, RT, air	
Entry	Light Source	Yield (%) <sup>b</sup>	dr <sup>c</sup>
1	450-470 nm	66	1:1
2	Blue LED	68	5:1
3	Purple LED	58	2:1
4	Green LED	62	5:1
5	White LED	55	2:1

Table S1. Screening of light source<sup>*a*</sup>

<sup>*a*</sup> Reaction conditions: **1a** (0.1 mmol), Rh-6G (2 mol%), FeSO<sub>4</sub>·7H<sub>2</sub>O (3 mol%), DCE (1.0 mL), LED light irradiation under air at room temperature for 16 h, then **2a** (0.15 mmol) and HI (15 mol%) were added and stirred under air at room temperature. <sup>*b*</sup> Yields were determined by <sup>1</sup>H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard. <sup>*c*</sup> Determined by <sup>1</sup>H NMR.

MeO	A DET + FeSO <sub>4</sub> ·7H <sub>2</sub> O, blue LED a 2a	, HI, Photocatalyst , DCE, RT, air	P N OEt S 3a
Entry	Photocatalyst	Yield (%) <i>b</i>	dr <sup>c</sup>
1 <i>d</i>	Rh-6G	57	4:1
2 <sup>e</sup>	Rh-6G	55	3:1
3	$Ru(bpy)_3Cl_2\cdot 6H_2O$	31	5.3:1
4	Eosin Y	trace	—
5	Victoria blue B	63	3:1
6	Eosin B	trace	_
7	Malachite Green	trace	_
8	Rhodamine B	35	5.3:1

## Table S2. Screening of photocatalyst<sup>a</sup>

<sup>*a*</sup> Reaction conditions: **1a** (0.1 mmol), photocatalyst (2 mol%), FeSO<sub>4</sub>·7H<sub>2</sub>O (3 mol%), DCE (1.0 mL), 18 W blue LED light irradiation under air at room temperature for 16 h, then **2a** (0.15 mmol) and HI (15 mol%) were added and stirred under air at room temperature. <sup>*b*</sup> Yields were determined by <sup>1</sup>H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard. <sup>*c*</sup> Determined by <sup>1</sup>H NMR. <sup>*d*</sup> 5 mol% Rh-6G was used. <sup>*e*</sup>10 mol% Rh-6G was used.

MeO	$\sim$ OEt + $\sim$ S FeSO <sub>4</sub> ·7H <sub>2</sub> O	o, HI, Photocatalyst	
ř N H 1a	blue LED,	, solvent, RT, air	
	<u> </u>		Ja 1. 0
Entry	Solvent	Y 1eld (%) <sup>b</sup>	dr <sup>c</sup>
1	CH <sub>3</sub> CN	68	> 20:1
2	DCE/CH <sub>3</sub> CN (10/1)	70	> 20:1
3	DCE/CH <sub>3</sub> CN (15/1)	78	> 20:1
4	DCE/CH <sub>3</sub> CN (20/1)	71	> 20:1
5	DCE/CH <sub>3</sub> CN (25/1)	82	> 20:1
6	DCE/CH <sub>3</sub> CN (30/1)	65	> 20:1
7	Toluene	ND	—
8	CH <sub>3</sub> OH	trace	—
9	CH <sub>3</sub> CH <sub>2</sub> OH	trace	
10	DMF	trace	—
11	DMAc	trace	—
12	DMSO	ND	_
13	THF	ND	—
14	Diethyl ether	ND	—
15	DCM	ND	—
16	1,4-dioxane	trace	—
17	CHCl <sub>3</sub>	58	> 20:1
18	TFA	ND	—
19	EtOAc	35	1.7:1
$20^d$	DCE/CH <sub>3</sub> CN (25/1)	44	> 20:1
21 <sup>e</sup>	DCE/CH <sub>3</sub> CN (25/1)	65	> 20:1
22 <sup>f</sup>	DCE/CH <sub>3</sub> CN (25/1)	70	9:1

### Table S3. Screening of solvents <sup>a</sup>

<sup>*a*</sup> Reaction conditions: **1a** (0.1 mmol), Rh-6G (2 mol%), FeSO<sub>4</sub>·7H<sub>2</sub>O (3 mol%), solvent (1.0 mL), 18 W blue LED light irradiation under air at room temperature for 16 h, then **2a** (0.15 mmol) and HI (15 mol%) were added and stirred under air at room temperature. <sup>*b*</sup> Yields were determined by <sup>1</sup>H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard. <sup>*c*</sup> Determined by <sup>1</sup>H NMR. <sup>*d*</sup> 3 mL DCE/CH<sub>3</sub>CN (25/1) was used. <sup>*e*</sup> 2 mL DCE/CH<sub>3</sub>CN (25/1) was used. <sup>*f*</sup> 0.5 mL DCE/CH<sub>3</sub>CN (25/1) was used.

## Table S4. Screening of Lewis acid <sup>a</sup>

MeO	$ \begin{array}{c}  \\  \\  \\  \\  \\  \\  \\  \\  \\  \\  \\  \\  \\ $	ewis acid, HI, Rh-6G DCE/CH <sub>3</sub> CN (25/1) blue LED, RT, air	P O N OEt S 3a
Entry	Lewis acid	Yield (%) <sup><i>b</i></sup>	dr <sup>c</sup>
$1^d$	FeSO <sub>4</sub> ·7H <sub>2</sub> O	79	> 20:1
2 <sup>e</sup>	FeSO <sub>4</sub> ·7H <sub>2</sub> O	86	> 20:1
3f	FeSO <sub>4</sub> ·7H <sub>2</sub> O	67	> 20:1
4	CuSO <sub>4</sub> ·5H <sub>2</sub> O	trace	—
5	Cu(OTf) <sub>2</sub>	39	> 20:1
6	Fe(OTf) <sub>2</sub>	48	> 20:1
7	Ce(OTf) <sub>3</sub>	53	> 20:1

<sup>*a*</sup> Reaction conditions: **1a** (0.1 mmol), Rh-6G (2 mol%), Lewis acid (3 mol%), DCE/CH<sub>3</sub>CN (25/1) (1.0 mL), 18 W blue LED light irradiation under air at room temperature for 16 h, then **2a** (0.15 mmol) and HI (15 mol%) were added and stirred under air at room temperature. <sup>*b*</sup> Yields were determined by <sup>1</sup>H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard. <sup>*c*</sup> Determined by <sup>1</sup>H NMR. <sup>*d*</sup> 10 mol% FeSO<sub>4</sub>·7H<sub>2</sub>O was used. <sup>*e*</sup> 20 mol% FeSO<sub>4</sub>·7H<sub>2</sub>O was used. <sup>*f*</sup> 30 mol% FeSO<sub>4</sub>·7H<sub>2</sub>O was used.

## Table S5. Screening the equivalent of 2a <sup>a</sup>

MeO NH H 1a	$V_{O}^{OEt} + V_{2a}^{S}$	FeSO <sub>4</sub> ·7H <sub>2</sub> O, HI, Rh-6G DCE/CH <sub>3</sub> CN (25/1) blue LED, RT, air	MP OEt
Entry	Equivalent	Yield (%) <sup>b</sup>	dr <sup>c</sup>
1	1.0	43	60:40
2	1.2	48	63:37
3	1.5	86	> 20:1

<sup>*a*</sup> Reaction conditions: **1a** (0.1 mmol), Rh-6G (2 mol%), FeSO<sub>4</sub>·7H<sub>2</sub>O (20 mol%), DCE/CH<sub>3</sub>CN (25/1), 18 W blue LED light irradiation under air at room temperature for 16 h, then **2a** and HI (15 mol%) were added and stirred under air at room temperature. <sup>*b*</sup> Yields were determined by <sup>1</sup>H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard. <sup>*c*</sup> Determined by <sup>1</sup>H NMR.

MeO N H 1a	OEt + F	eSO <sub>4</sub> ·7H <sub>2</sub> O, HI, Rh-6G DCE/CH <sub>3</sub> CN (25/1) blue LED, RT, air	MP, OEt V OEt 3a
Entry	Equivalent	Yield (%) <sup>b</sup>	dr <sup>c</sup>
1	0.05	44	89:11
2	0.1	55	95:5
3	0.15	86	> 20:1
4	0.25	66	92:8

Table S6.	Screening	the eq	uivalent	of HI a

<sup>*a*</sup> Reaction conditions: **1a** (0.1 mmol), Rh-6G (2 mol%), FeSO<sub>4</sub>·7H<sub>2</sub>O (20 mol%), DCE/CH<sub>3</sub>CN (25/1) (1 mL), 18 W blue LED light irradiation under air at room temperature for 16 h, then **2a** (0.15 mmol) and HI were added and stirred under air at room temperature. <sup>*b*</sup> Yields were determined by <sup>1</sup>H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard. <sup>*c*</sup> Determined by <sup>1</sup>H NMR.

## 3. Mechanistic Investigation

## 3.1 Control experiments



Scheme S3 Control experiment.

## 3.2 Cyclic voltammetry experiments

Cyclic Voltammetry was performed on a CH Instruments Electrochemical Workstation model CHI760E. A solution of **1a** or **1a-FeSO**<sub>4</sub>·**7H**<sub>2</sub>**O** in DCE ( $2 \times 10^{-7}$  M) was tested with 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> as the supporting electrolyte, using a glassy carbon as the working electrode, a Pt as the counter electrode, and a saturated calomel electrode reference electrode. Scan rate = 0.05 V/s, 1 sweep segments, a sample interval of 0.001 V.



Fig. S3 Cyclic Voltammetry of 1a and  $1a\text{-}FeSO_4\text{-}7H_2O$  in DCE

#### 3.3 UV/Vis absorption spectra

The UV/Vis absorption spectra were recorded in 1 cm path quartz cuvettes by using a Varian Cary 300 Conc UV/Vis spectrometer. Sample preparation method: **1a** (0.125 mmol) was dissolved in 10 mL DCE, then the solution was divided into two parts, FeSO<sub>4</sub>·7H<sub>2</sub>O (20 mol%) was added to one of them and ultrasonic treatment was performed for 60 min.



Fig. S4 The UV-Vis spectra of 1a and 1a + FeSO<sub>4</sub>·7H<sub>2</sub>O

## 3.4 EPR spectra



**Fig. S5** EPR spectra of **1a** (0.1 M), Rh-6G ( $1 \times 10^{-3}$  M) and DMPO (0.05 M) or TEMP (0.5 M) in air-saturated DCE upon irradiation with blue LED for 100 s. These results illustrate that O<sub>2</sub><sup>--</sup> generated from molecular oxygen is the primary active species in this photocatalytic oxidative reaction.

## 3.5 Stern-Volmer fluorescence quenching study

DCE was degassed with a stream of argon for 30 min. Rh-6G was dissolved in 10.0 mL DCE to prepare a  $1.0 \times 10^{-7}$  M solution. 0.1 mL of this solution was added to each of a set of 6 volumetric flasks (10 mL). Subsequently, the solution of quencher **1a** in DCE (1.0 mL,  $2 \times 10^{-3}$  M) was added in increasing amounts to the volumetric flasks, emission intensities were recorded.



Fig. S6 Changes in the fluorescence spectra



Fig. S7 Stern-Volmer Plot

## 4. Computational Study

## 4.1 Computational methods

All calculations were carried out with the Gaussian 09 D.01programs.<sup>3</sup> Ground state geometry were fully optimized by using density functional theory (DFT)<sup>4</sup> and the B3LYP<sup>5</sup>-D3 method with the 6-31G(d,p) basis set for C, H, O, N, S atoms and Lanl2DZ for Fe atom. Frequency calculations have been performed. The 3D molecular structures were generated using the CYL-view.<sup>6</sup> Using this geometry (singlet and triplet), single point time dependent density functional theory (TD-DFT) calculation was then performed using the CAM-B3LYP-D3/6-31G(d,p)/Lanl2DZ level of theory. The effect of solvent is considered from Truhlar and co-workers' universal solvation model (SMD<sup>7</sup>-DCE).

#### 4.2 Optimized structure of 1a+ FeSO<sub>4</sub>



**Optimized structure of 1a and 1a + FeSO<sub>4</sub>** 

	1a	FeSO <sub>4</sub>	1a + FeSO <sub>4</sub>	ΔE	$\Delta \mathrm{E}/\mathrm{kcal}$ mol $^{-1}$
ZPE	-708.19	-822.16	-1530.46	-0.11	-69.03
Enthalpy	-708.17	-822.15	-1530.44	-0.12	-75.30
Gibbs	-708.24	-822.19	-1530.52	-0.09	-56.48

\* Unmarked energies in the table are given in Hartree.

## 4.3 Theory predicts UV-Vis spectrum of 1a and 1a+ FeSO<sub>4</sub>



Fig. S8 Theory predicts UV/Vis absorption spectra

## 4.4 The relative energies of the *cis-* and *trans-*products



## 4.5 The Cartesian Coordinates

1	a
0	1

С	-3.66387600	0.15410200	0.06597200
С	-3.08731000	1.43408700	0.07533000
С	-1.70875800	1.58472400	0.01303900
С	-0.85608100	0.45661700	-0.06072800
С	-1.44624900	-0.82086400	-0.06985900
С	-2.84008100	-0.97090400	-0.00686800
Н	-3.74322400	2.29510400	0.13194900

Н	-1.27449300	2.58051000	0.02084500
Н	-0.82962700	-1.71078000	-0.12524100
Н	-3.25663600	-1.97088700	-0.01602000
0	-5.06197100	0.12069800	0.13277100
С	-5.71372200	-1.17210200	0.12935000
Н	-5.40980200	-1.77755700	0.99358700
Н	-6.78103400	-0.95912700	0.18909600
Н	-5.49995400	-1.72754800	-0.79348800
С	2.86859800	0.09777100	-0.25005500
0	3.16605400	1.29857100	-0.21559000
0	3.78120400	-0.91395200	-0.33827000
С	5.22128100	-0.53976400	-0.37540100
Н	5.33049400	0.33280000	-1.02514900
Н	5.69389700	-1.40997600	-0.83233300
С	5.73648800	-0.26384900	1.02952100
Н	5.55948700	-1.12475100	1.68152400
Н	6.81445900	-0.06764800	0.99972100
Н	5.23873900	0.61295600	1.45294300
Ν	0.51986500	0.63691900	-0.12095500
Н	0.90906900	1.56794900	-0.10912000
С	1.46074000	-0.44890400	-0.20277800
Н	1.30803800	-1.07451900	-1.09793400
Н	1.39306200	-1.13297100	0.65987300

## 1a + FeSO<sub>4</sub>

05		
С	4.01031600 -0.4	4021500 -0.05643900
С	3.18058200 -1.5	7362800 0.01259600
С	1.83889600 -1.4	4090000 0.34105400

С	1.30610600	-0.16408100	0.61300800
С	2.12635900	0.96402000	0.53589300
С	3.48330800	0.82915700	0.20162100
Н	3.61241500	-2.54414300	-0.19840500
Н	1.18250000	-2.30372100	0.37368300
Н	1.73953000	1.95732800	0.73892100
Н	4.10335000	1.71519100	0.15301200
0	5.33498500	-0.69102700	-0.39114000
С	6.25669300	0.42739800	-0.48021300
Н	6.34356800	0.94874700	0.48124100
Н	7.21618900	-0.01343200	-0.74741800
Н	5.94646900	1.13768200	-1.25677500
С	-0.96078200	2.13304500	0.39727600
0	-1.15525800	1.75870900	-0.79407800
0	-1.04992800	3.40020200	0.78258500
С	-1.49545400	4.44140700	-0.21573100
Н	-0.96882000	4.24218300	-1.15162000
Н	-1.13847900	5.36526500	0.23728900
С	-3.00532700	4.39457600	-0.37259100
Н	-3.50181800	4.52830400	0.59264000
Н	-3.32527800	5.20325800	-1.03902900
Н	-3.32452500	3.44514700	-0.81136600
Ν	-0.10767200	-0.08543500	0.90702100
Н	-0.45996400	-0.94351900	1.37706700
Fe	-1.24541400	-0.31260000	-0.99211500
S	-2.23017300	-2.54039800	0.16083600
0	-1.34311400	-2.57710400	1.55743900
0	-1.07380300	-2.24528000	-1.16087400
0	-2.89693700	-0.92042600	0.00359600

С	-0.64675600	1.14353100	1.50063700
Н	0.00714300	1.60362100	2.24837700
Н	-1.59918600	0.88482200	1.98012000
0	-3.26338100	-3.74264700	-0.11851900

# 5. X-ray Crystal Structure for Compound 3m and 8a

Empirical formula	C <sub>18</sub> H <sub>18</sub> INO <sub>2</sub> S
Formula weight	439.29
Temperature/K	150.00(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	8.96313(11)
b/Å	6.06546(8)
c/Å	32.0458(3)
α/°	90
β/°	91.1858(10)
γ/ <sup>0</sup>	90
Volume/Å <sup>3</sup>	1741.81(4)
Z	4
ρ <sub>calc</sub> g/cm <sup>3</sup>	1.675
μ/mm <sup>-1</sup>	15.635
F(000)	872.0
Crystal size/mm <sup>3</sup>	0.12  imes 0.08  imes 0.07
Radiation	Cu Ka ( $\lambda = 1.54184$ )
20 range for data collection/	° 5.516 to 154.948
Index ranges	$-11 \le h \le 11, -7 \le k \le 7, -24 \le l \le 40$
<b>Reflections collected</b>	10301
Independent reflections	3442 [ $R_{int} = 0.0471, R_{sigma} = 0.0401$ ]
Data/restraints/parameters	3442/0/209
Goodness-of-fit on F <sup>2</sup>	1.064
Final R indexes [I>=2σ (I)]	$R_1 = 0.0412, wR_2 = 0.1161$
Final R indexes [all data]	$R_1 = 0.0421, wR_2 = 0.1172$
Largest diff. peak/hole / e Å <sup>-3</sup>	1.12/-1.38



Empirical formula	$C_{19}H_{21}NO_4S$
Formula weight	338.51
Temperature/K	149.99(10)
Crystal system	monoclinic
Space group	P21/n
a/Å	6.61353(9)
b/Å	27.3767(4)
c/Å	10.14913(14)
α /°	90
β /°	104.4142(14)
γ /°	90
Volume/Å <sup>3</sup>	1779.73(4)
Z	4
ρ calcg/cm <sup>3</sup>	1.263
μ /mm <sup>-1</sup>	1.813
F(000)	677.0
Crystal size/mm <sup>3</sup>	0.18  imes 0.16  imes 0.12
Radiation	Cu K $\alpha$ ( $\lambda$ = 1.54184)
$2 \Theta$ range for data collection/°	6.458 to 155.174
Index ranges	$\textbf{-6} \leqslant \textbf{h} \leqslant \textbf{8}, \textbf{-33} \leqslant \textbf{k} \leqslant \textbf{31}, \textbf{-12} \leqslant \textbf{1}$
mura ranges	≤ 12
Reflections collected	11436
	S24

Indon on dont well astions	3576 [Rint = 0.0424, Rsigma =
Independent reflections	0.0420]
Data/restraints/parameters	3576/0/229
Goodness-of-fit on F <sup>2</sup>	1.068
Final R indexes [I>=2σ (I)]	R1 = 0.0406, wR2 = 0.1101
Final R indexes [all data]	R1 = 0.0437, wR2 = 0.1125
Largest diff. peak/hole / e Å <sup>-3</sup>	0.41/-0.51

## 6. Product Data



*Ethyl 3-(4-methoxyphenyl)-4-phenylthiazolidine-2-carboxylate* (*3a*). Purified by flash column chromatography (silica gel, PE/EA = 64/1 to 16/1 as eluent). Colorless oily liquid, 83 % yield, > 20:1 dr. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.35-7.26 (m, 5H), 6.71 (d, *J* = 9.1 Hz, 2H), 6.46 (d, *J* = 9.2 Hz, 2H), 5.38 (s, 1H), 5.27 (dd, *J* = 7.2, 1.6 Hz, 1H), 4.30-4.17 (m, 2H), 3.98 (dd, *J* = 11.2, 7.2 Hz, 1H), 3.68 (s, 3H), 2.90 (dd, *J* = 11.2, 1.5 Hz, 1H), 1.28 (t, *J* = 7.1 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  171.9, 152.3, 142.6, 138.8, 128.7, 127.6, 126.5, 115.0, 114.9, 66.0, 64.1, 61.7, 55.7, 39.3, 14.3. HRMS (ESI) calcd for C<sub>19</sub>H<sub>22</sub>NO<sub>3</sub>S (M+H<sup>+</sup>) 344.1315, found 344.1316.



*Ethyl* 3,4-diphenylthiazolidine-2-carboxylate (3b). Purified by flash column chromatography (silica gel, PE/EA = 64/1 to 16/1 as eluent). Light red oily liquid, 58 % yield, > 20:1 dr. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.35-7.26 (m, 5H), 7.16-7.08 (m, 2H), 6.72-6.68 (m, 1H), 6.50-6.45 (m, 2H), 5.39 (s, 1H), 5.32 (d, *J* = 7.5 Hz, 1H), 4.32-4.16 (m, 2H), 4.01 (dd, *J* = 11.3, 7.1 Hz, 1H), 2.90 (dd, *J* = 11.2, 1.0 Hz, 1H), 1.29 (t, *J* = 7.1 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  171.7, 144.4, 142.3, 129.4, 128.7, 127.7, 126.4, 118.1, 113.6, 65.9, 63.6, 61.8, 39.3, 14.3. HRMS (ESI) calcd for C<sub>18</sub>H<sub>20</sub>NO<sub>2</sub>S

(M+H<sup>+</sup>) 314.1209, found 314.1210.



*Ethyl 4-phenyl-3-(p-tolyl)thiazolidine-2-carboxylate (3c).* Purified by flash column chromatography (silica gel, PE/EA = 64/1 to 16/1 as eluent). White solid, 62 % yield, > 20:1 dr. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.25-7.19 (m, 5H), 6.90-6.82 (m, 2H), 6.37-6.29 (m, 2H), 5.31 (s, 1H), 5.22 (dd, *J* = 7.2, 1.1 Hz, 1H), 4.26-4.07 (m, 2H), 3.93 (dd, *J* = 11.2, 7.2 Hz, 1H), 2.82 (dd, *J* = 11.2, 1.2 Hz, 1H), 2.11 (s, 3H), 1.22 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  171.8, 142.5, 142.2, 129.9, 128.7, 127.6, 127.1, 126.4, 113.7, 65.8, 63.7, 61.7, 39.3, 20.3, 14.3. HRMS (ESI) calcd for C<sub>19</sub>H<sub>22</sub>NO<sub>2</sub>S (M+H<sup>+</sup>) 328.1366, found 328.1365.



*Ethyl 3-(4-ethylphenyl)-4-phenylthiazolidine-2-carboxylate (3d).* Purified by flash column chromatography (silica gel, PE/EA = 64/1 to 16/1 as eluent). White solid, 71 % yield, > 20:1 dr. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.32 (d, *J* = 4.3 Hz, 4H), 7.26-7.23 (m, 1H), 6.95 (d, *J* = 8.6 Hz, 2H), 6.41 (d, *J* = 8.6 Hz, 2H), 5.38 (s, 1H), 5.29 (d, *J* = 7.1 Hz, 1H), 4.33-4.15 (m, 2H), 4.00 (dd, *J* = 11.2, 7.2 Hz, 1H), 2.89 (dd, *J* = 11.3, 1.1 Hz, 1H), 2.48 (q, *J* = 7.6 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.13 (t, *J* = 7.6 Hz, 3H);<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  171.9, 142.6, 142.4, 133.6, 128.74, 128.69, 127.6, 126.5, 113.6, 65.9, 63.7, 61.7, 39.3, 27.8, 15.7, 14.3. HRMS (ESI) calcd for C<sub>20</sub>H<sub>24</sub>NO<sub>2</sub>S (M+H<sup>+</sup>) 342.1522, found 342.1524.



*Ethyl 3-(4-isopropylphenyl)-4-phenylthiazolidine-2-carboxylate* (*3e*). Purified by flash column chromatography (silica gel, PE/EA = 64/1 to 16/1 as eluent). White solid, 72 % yield, > 20:1 dr. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.25-7.18 (m, 5H), 6.93-6.86 (m, 2H), 6.36-6.30 (m, 2H), 5.29 (s, 1H), 5.20 (d, *J* = 7.0 Hz, 1H), 4.25-4.07 (m, 2H), 3.92 (dd, *J* = 11.2, 7.2 Hz, 1H), 2.80 (dd, *J* = 11.2, 1.0 Hz, 1H), 2.67 (hept, *J* = 6.9 Hz, 1H), 1.21 (t, *J* = 7.1 Hz, 3H), 1.07 (dd, *J* = 6.9, 1.4 Hz, 6H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  171.9, 142.7, 142.4, 138.2, 128.7, 127.6, 127.3, 126.5, 113.5, 66.0, 63.7, 61.7, 39.3, 33.1, 24.2, 24.8, 14.3. HRMS (ESI) calcd for C<sub>21</sub>H<sub>26</sub>NO<sub>2</sub>S (M+H<sup>+</sup>) 356.1679, found 356.1680.



*Ethyl 3-(4-butylphenyl)-4-phenylthiazolidine-2-carboxylate (3f).* Purified by flash column chromatography (silica gel, PE/EA = 64/1 to 16/1 as eluent). White solid, 48 % yield, > 20:1 dr. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.32-7.27 (m, 5H), 6.96-6.89 (m, 2H), 6.43-6.36 (m, 2H), 5.37 (s, 1H), 5.28 (d, *J* = 7.1 Hz, 1H), 4.31-4.16 (m, 2H), 4.00 (dd, *J* = 11.2, 7.2 Hz, 1H), 2.88 (dd, *J* = 11.2, 1.1 Hz, 1H), 2.48-2.40 (m, 2H), 1.53-1.44 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 5H), 0.88 (t, *J* = 7.3 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  171.7, 142.5, 142.2, 132.2, 129.1, 128.5, 127.4, 126.3, 113.4, 65.8, 63.6, 61.6, 39.2, 34.5, 33.7, 22.3, 14.1, 13.9. HRMS (ESI) calcd for C<sub>22</sub>H<sub>28</sub>NO<sub>2</sub>S (M+H<sup>+</sup>) 370.1835, found 370.1830.



*Ethyl 3-(4-(tert-butyl)phenyl)-4-phenylthiazolidine-2-carboxylate (3g).* Purified by flash column chromatography (silica gel, PE/EA = 64/1 to 16/1 as eluent). White solid, 30 % yield, > 20:1 dr. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.36-7.26 (m, 5H), 7.18-7.11 (m, 2H), 6.45-6.39 (m, 2H), 5.38 (s, 1H), 5.29 (d, *J* = 7.0 Hz, 1H), 4.34-4.16 (m, 2H), 4.01 (dd, *J* = 11.2, 7.2 Hz, 1H), 2.88 (dd, *J* = 11.3, 1.0 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.22 (s, 9H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  171.7, 142.6, 141.9, 140.4, 128.6, 127.5, 126.3, 126.1, 113.1, 65.9, 63.6, 61.6, 39.2, 33.6, 31.4, 14.1. HRMS (ESI) calcd for C<sub>22</sub>H<sub>28</sub>NO<sub>2</sub>S (M+H<sup>+</sup>) 370.1835, found 370.1832.



*Ethyl 3-(4-ethoxyphenyl)-4-phenylthiazolidine-2-carboxylate* (*3h*). Purified by flash column chromatography (silica gel, PE/EA = 64/1 to 16/1 as eluent). White solid, 81 % yield, > 20:1 dr. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.26-7.24 (m, 3H), 7.24-7.15 (m, 2H), 6.69-6.59 (m, 2H), 6.43-6.33 (m, 2H), 5.31 (s, 1H), 5.19 (dd, *J* = 7.2, 1.5 Hz, 1H), 4.23-4.07 (m, 2H), 3.91 (dd, *J* = 11.1, 7.2 Hz, 1H), 3.83 (q, *J* = 7.0 Hz, 2H), 2.83 (dd, *J* = 11.2, 1.6 Hz, 1H), 1.26 (t, *J* = 7.0 Hz, 3H), 1.21 (t, *J* = 7.1 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  171.9, 151.6, 142.6, 138.7, 128.7, 127.6, 126.5, 115.7, 115.0, 66.0, 64.1, 63.9, 61.7, 39.3, 15.1, 14.3. HRMS (ESI) calcd for C<sub>20</sub>H<sub>24</sub>NO<sub>3</sub>S (M+H<sup>+</sup>) 358.1471, found 358.1474.



*Ethyl 3-(4-phenoxyphenyl)-4-phenylthiazolidine-2-carboxylate (3i).* Purified by flash column chromatography (silica gel, PE/EA = 64/1 to 16/1 as eluent). White solid, 73 % yield, > 20:1 dr. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.27 (s, 2H), 7.25-7.19 (m, 2H), 7.18 (d, *J* = 1.9 Hz, 2H), 7.16 (d, *J* = 1.8 Hz, 1H), 6.95-6.90 (m, 1H), 6.84-6.81 (m, 2H), 6.79-6.73 (m, 2H), 6.42-6.37 (m, 2H), 5.31 (s, 1H), 5.25-5.19 (m, 1H), 4.24-4.12 (m, 2H), 3.94 (dd, *J* = 11.3, 7.2 Hz, 1H), 2.83 (dd, *J* = 11.2, 1.2 Hz, 1H), 1.22 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  171.6, 158.5, 148.3, 142.2, 140.9, 129.5, 128.7, 127.6, 126.3, 122.3, 120.8, 117.6, 114.5, 66.1, 63.8, 61.7, 39.2, 14.2. HRMS (ESI) calcd for C<sub>24</sub>H<sub>24</sub>NO<sub>3</sub>S (M+H<sup>+</sup>) 406.1393, found 406.1388.



*Ethyl 3-(4-fluorophenyl)-4-phenylthiazolidine-2-carboxylate (3j).* Purified by flash column chromatography (silica gel, PE/EA = 64/1 to 16/1 as eluent). White solid, 91 % yield, > 20:1 dr. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.36-7.26 (m, 5H), 6.87-6.79 (m, 2H), 6.45-6.38 (m, 2H), 5.36 (s, 1H), 5.26 (dd, *J* = 7.2, 1.3 Hz, 1H), 4.33-4.17 (m, 2H), 3.99 (dd, *J* = 11.2, 7.2 Hz, 1H), 2.90 (dd, *J* = 11.2, 1.3 Hz, 1H), 1.28 (t, *J* = 7.1 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  171.6, 156.1 (d, *J* = 237.8 Hz), 142.1, 140.9 (d, *J* = 1.9 Hz), 128.8, 127.8, 126.4, 115.9 (d, *J* = 22.4 Hz), 114.6 (d, *J* = 7.5 Hz), 66.2, 64.0, 61.9, 39.3, 14.3. HRMS (ESI) calcd for C<sub>18</sub>H<sub>19</sub>FNO<sub>2</sub>S (M+H<sup>+</sup>) 332.1115, found 332.1116.



*Ethyl 3-(4-chlorophenyl)-4-phenylthiazolidine-2-carboxylate (3k).* Purified by flash column chromatography (silica gel, PE/EA = 64/1 to 16/1 as eluent). White solid, 66 % yield, > 20:1 dr. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.31-7.19 (m, 5H), 7.18-7.12 (m, 2H), 6.33-6.27 (m, 2H), 5.29 (s, 1H), 5.22 (d, *J* = 7.1 Hz, 1H), 4.28-4.11 (m, 2H), 3.95 (dd,

J = 11.3, 7.1 Hz, 1H), 2.85 (dd, J = 11.3, 1.0 Hz, 1H), 1.24 (t, J = 7.1 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  171.3, 143.4, 141.7, 132.1, 128.8, 127.8, 126.3, 115.2, 110.3, 66.0, 63.6, 62.0, 39.2, 14.3. HRMS (ESI) calcd for C<sub>18</sub>H<sub>19</sub>ClNO<sub>2</sub>S (M+H<sup>+</sup>) 348.0820, found 348.0821.



*Ethyl 3-(4-bromophenyl)-4-phenylthiazolidine-2-carboxylate (3i).* Purified by flash column chromatography (silica gel, PE/EA = 64/1 to 16/1 as eluent). White solid, 43 % yield, > 20:1 dr. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.32-7.19 (m, 5H), 7.05-6.98 (m, 2H), 6.38-6.32 (m, 2H), 5.30 (s, 1H), 5.22 (d, *J* = 7.1 Hz, 1H), 4.28-4.11 (m, 2H), 3.95 (dd, *J* = 11.3, 7.1 Hz, 1H), 2.85 (d, *J* = 11.3 Hz, 1H), 1.24 (t, *J* = 7.1 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  171.3, 143.0, 141.8, 129.3, 128.8, 127.8, 126.4, 123.1, 114.7, 66.0, 63.6, 61.9, 39.2, 14.3. HRMS (ESI) calcd for C<sub>18</sub>H<sub>19</sub>BrNO<sub>2</sub>S (M+H<sup>+</sup>) 392.0314, found 392.0318.



*Ethyl 3-(4-iodophenyl)-4-phenylthiazolidine-2-carboxylate (3m).* Purified by flash column chromatography (silica gel, PE/EA = 64/1 to 16/1 as eluent). White solid, 51 % yield, > 20:1 dr. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.35-7.30 (m, 2H), 7.30-7.20 (m, 5H), 6.21-6.19 (m, 2H), 5.29 (s, 1H), 5.22 (d, *J* = 7.0 Hz, 1H), 4.26-4.12 (m, 7.1 Hz, 2H), 3.95 (dd, *J* = 11.3, 7.2 Hz, 1H), 2.85 (dd, *J* = 11.3, 1.0 Hz, 1H), 1.25 (t, *J* = 7.1 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  171.3, 144.0, 141.6, 138.0, 128.8, 127.9, 126.3, 115.9, 79.7, 65.9, 63.4, 62.0, 39.2, 14.3. HRMS (ESI) calcd for C<sub>18</sub>H<sub>19</sub>INO<sub>2</sub>S (M+H<sup>+</sup>) 440.1076, found 440.1076.



*Ethyl 3-(3-fluoro-4-methylphenyl)-4-phenylthiazolidine-2-carboxylate (3n).* Purified by flash column chromatography (silica gel, PE/EA = 64/1 to 16/1 as eluent). White solid, 46 % yield, > 20:1 dr. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.37-7.26 (m, 5H), 6.90 (t, J = 8.5 Hz, 1H), 6.21-6.11 (m, 2H), 5.34 (s, 1H), 5.26 (d, J = 7.1 Hz, 1H), 4.35-4.16 (m, 2H), 4.00 (dd, J = 11.3, 7.2 Hz, 1H), 2.89 (dd, J = 11.4, 1.1 Hz, 1H), 2.09 (d, J = 1.8 Hz, 3H), 1.30 (t, J = 7.1 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  171.4, 161.9 (d, J = 243.3 Hz), 144.0 (d, J = 10.5 Hz), 142.0, 131.9 (d, J = 7.1 Hz), 128.8, 127.8, 126.4, 113.7 (d, J = 17.8 Hz), 109.1 (d, J = 2.8 Hz), 101.0 (d, J = 28.0 Hz), 66.0, 63.6, 61.9, 39.2, 14.3, 13.6 (d, J = 3.1 Hz). HRMS (ESI) calcd for C<sub>19</sub>H<sub>21</sub>FNO<sub>2</sub>S (M+H<sup>+</sup>) 346.1272, found 346.1274.



*Benzyl 3-(4-methoxyphenyl)-4-phenylthiazolidine-2-carboxylate (30).* Purified by flash column chromatography (silica gel, PE/EA = 64/1 to 16/1 as eluent). White solid, 73 % yield, > 20:1 dr. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.33-7.17 (m, 10H), 6.65-6.56 (m, 2H), 6.44-6.34 (m, 2H), 5.38 (s, 1H), 5.22-5.18 (m, 1H), 5.19-5.07 (m, 2H), 3.89 (dd, J = 11.2, 7.2 Hz, 1H), 3.62 (s, 3H), 2.82 (dd, J = 11.2, 1.6 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  171.7, 152.3, 142.5, 138.7, 135.6, 128.69, 128.67, 128.4, 128.2, 127.6, 126.4, 115.0, 114.9, 67.2, 66.0, 64.2, 55.7, 39.3. HRMS (ESI) calcd for C<sub>24</sub>H<sub>24</sub>NO<sub>3</sub>S (M+H<sup>+</sup>) 406.1471, found 406.1474.



*Butyl 3-(4-methoxyphenyl)-4-phenylthiazolidine-2-carboxylate (3p).* Purified by flash column chromatography (silica gel, PE/EA = 64/1 to 16/1 as eluent). White solid, 77 % yield, > 20:1 dr. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.29-7.16 (m, 5H), 6.68-6.59 (m, 2H), 6.44-6.34 (m, 2H), 5.32 (s, 1H), 5.19 (dd, *J* = 7.3, 1.5 Hz, 1H), 4.11-4.08 (m, 2H), 3.91 (dd, *J* = 11.2, 7.2 Hz, 1H), 3.61 (s, 3H), 2.83 (dd, *J* = 11.1, 1.5 Hz, 1H), 1.55 (m, 2H), 1.35-1.23 (m, 2H), 0.85 (t, *J* = 7.4 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  172.0, 152.7, 142.6, 138.8, 128.7, 127.6, 126.5, 114.93, 114.91, 66.0, 65.5, 64.2, 55.7, 39.3, 30.7, 19.1, 13.8. HRMS (ESI) calcd for C<sub>21</sub>H<sub>26</sub>NO<sub>3</sub>S (M+H<sup>+</sup>) 372.1628, found 372.1625.



*Cyclopropylmethyl* 3-(4-methoxyphenyl)-4-phenylthiazolidine-2-carboxylate (3q). Purified by flash column chromatography (silica gel, PE/EA = 64/1 to 16/1 as eluent). Yellow solid, 86 % yield, > 20:1 dr. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.26-7.16 (m, 5H), 6.67-6.60 (m, 2H), 6.43-6.37 (m, 2H), 5.33 (s, 1H), 5.19 (dd, *J* = 7.2, 1.5 Hz, 1H), 4.03-3.83 (m, 3H), 3.61 (s, 3H), 2.83 (dd, *J* = 11.2, 1.5 Hz, 1H), 1.20 (s, 1H), 1.13-1.01 (m, 1H), 0.53-0.45 (m, 2H), 0.25-0.17 (m, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  172.0, 152.2, 142.6, 138.8, 128.7, 127.6, 126.5, 114.94, 114.88, 70.3, 66.0, 64.2, 55.7, 39.3, 9.9, 3.4, 3.4. HRMS (ESI) calcd for C<sub>21</sub>H<sub>24</sub>NO<sub>3</sub>S (M+H<sup>+</sup>) 370.1471, found 370.1475.



*Cyclobutylmethyl* 3-(4-methoxyphenyl)-4-phenylthiazolidine-2-carboxylate (3r). Purified by flash column chromatography (silica gel, PE/EA = 64/1 to 16/1 as eluent). White solid, 72 % yield, > 20:1 dr. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.27-7.16 (m, 5H),

6.67-6.61 (m, 2H), 6.42-6.36 (m, 2H), 5.33 (s, 1H), 5.17 (dd, J = 7.3, 1.5 Hz, 1H), 4.12-4.02 (m, 2H), 3.91 (dd, J = 11.1, 7.3 Hz, 1H), 3.61 (s, 3H), 2.83 (dd, J = 11.2, 1.5 Hz, 1H), 2.56 (hept, J = 7.3 Hz, 1H), 2.01-1.89 (m, 2H), 1.88-1.59 (m, 4H), 1.39-1.17 (m, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  172.2, 152.3, 142.6, 138.8, 128.7, 127.6, 126.5, 114.94, 114.90, 69.2, 66.0, 64.2, 55.7, 39.3, 34.2, 24.7, 24.7, 18.5. HRMS (ESI) calcd for C<sub>22</sub>H<sub>26</sub>NO<sub>3</sub>S (M+H<sup>+</sup>) 384.1628, found 384.1627.



*Cyclohexyl 3-(4-methoxyphenyl)-4-phenylthiazolidine-2-carboxylate (3s).* Purified by flash column chromatography (silica gel, PE/EA = 64/1 to 16/1 as eluent). White solid, 80 % yield, > 20:1 dr. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.38-7.26 (m, 5H), 6.75-6.68 (m, 2H), 6.50-6.44 (m, 2H), 5.38 (s, 1H), 5.25 (dd, *J* = 7.3, 1.5 Hz, 1H), 4.88-4.82 (m, 1H), 4.00 (dd, *J* = 11.1, 7.3 Hz, 1H), 3.69 (s, 3H), 2.90 (dd, *J* = 11.1, 1.5 Hz, 1H), 1.90-1.82 (m, 1H), 1.81-1.68 (m, 2H), 1.65-1.49 (m, 3H), 1.45-1.28 (m, 4H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  171.3, 152.2, 142.6, 138.8, 128.6, 127.5, 126.4, 114.89, 114.85, 73.8, 66.0, 64.4, 55.6, 39.2, 31.5, 31.1, 25.3, 23.5, 23.3. HRMS (ESI) calcd for C<sub>23</sub>H<sub>28</sub>NO<sub>3</sub>S (M+H<sup>+</sup>) 398.1784, found 398.1790.



*Cycloheptyl 3-(4-methoxyphenyl)-4-phenylthiazolidine-2-carboxylate (3t).* Purified by flash column chromatography (silica gel, PE/EA = 64/1 to 16/1 as eluent). White solid, 78 % yield, > 20:1 dr. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.27-7.16 (m, 5H), 6.68-6.59 (m, 2H), 6.43-6.34 (m, 2H), 5.28 (s, 1H), 5.16 (dd, *J* = 7.3, 1.5 Hz, 1H), 4.94-4.88 (m, 1H), 3.91 (dd, *J* = 11.1, 7.3 Hz, 1H), 3.61 (s, 3H), 2.81 (dd, *J* = 11.1, 1.5 Hz, 1H), 1.88-1.83 (m, 1H), 1.75-1.31 (m, 12H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  171.3, 152.2, 142.7, 138.9, 128.7, 127.6, 126.4, 114.90, 114.87, 76.6, 66.1, 64.5, 55.7, 39.3, 33.9,

33.5, 28.30, 28.29, 23.0, 22.8. HRMS (ESI) calcd for  $C_{24}H_{30}NO_3S$  (M+H<sup>+</sup>) 412.1941, found 412.1946.



*N-cyclohexyl-3-(4-methoxyphenyl)-4-phenylthiazolidine-2-carboxamide* (*3u*). Purified by flash column chromatography (silica gel, PE/EA = 64/1 to 16/1 as eluent). White solid, 60 % yield, > 20:1 dr. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.30-7.22 (m, 3H), 7.16-7.10 (m, 2H), 6.72-6.66 (m, 2H), 6.52-6.46 (m, 2H), 6.17 (d, *J* = 8.7 Hz, 1H), 5.44 (d, *J* = 5.9 Hz, 1H), 5.19 (s, 1H), 3.83-3.73 (m, 2H), 3.68 (s, 3H), 2.93 (dd, *J* = 11.3, 1.3 Hz, 1H), 1.91 (dd, *J* = 12.6, 4.3 Hz, 1H), 1.83-1.72 (m, 1H), 1.72-1.52 (m, 3H), 1.43-1.27 (m, 2H), 1.19-1.04 (m, 2H), 1.03-0.84 (m, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$ 170.5, 152.8, 140.4, 138.0, 128.5, 127.7, 126.9, 116.2, 114.8, 66.8, 66.7, 55.6, 48.3, 38.5, 33.1, 32.8, 25.5, 24.9, 24.7. HRMS (ESI) calcd for C<sub>23</sub>H<sub>29</sub>N<sub>2</sub>O<sub>2</sub>S (M+H<sup>+</sup>) 397.1944, found 397.1949.



2-(((*E*)-3,7-dimethylocta-2,6-dien-1-yl)oxy)-1-((2*R*,4*S*)-3-(4-methoxyphenyl)-4phenylthiazolidin-2-yl)ethan-1-one (3v). Purified by flash column chromatography (silica gel, PE/EA = 64/1 to 16/1 as eluent). White solid, 78% yield, > 20:1 dr. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.35-7.22 (m, 5H), 6.74-6.67 (m, 2H), 6.48-6.42 (m, 2H), 5.40-5.29 (m, 2H), 5.26 (dd, *J* = 7.3, 1.5 Hz, 1H), 5.12-5.08 (m, 1H), 4.77-4.59 (m, 2H), 3.98 (dd, *J* = 11.1, 7.2 Hz, 1H), 3.68 (s, 3H), 2.89 (dd, *J* = 11.2, 1.5 Hz, 1H), 2.16-2.01 (m, 4H), 1.70 (dd, *J* = 3.6, 1.4 Hz, 6H), 1.62 (d, *J* = 1.3 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  171.9, 152.3, 143.4, 142.6, 138.8, 132.0, 128.7, 127.6, 126.5, 123.8, 117.8, 115.0, 114.9, 66.0, 64.1, 62.5, 55.7, 39.6, 39.3, 26.4, 25.8, 17.8, 16.7. HRMS (ESI) calcd for C<sub>27</sub>H<sub>34</sub>NO<sub>3</sub>S (M+H<sup>+</sup>) 452.2254, found 452.2255.



((3aS,5aR,8aR,8bS)-2,2,7,7-tetramethyltetrahydro-3aH-bis([1,3]dioxolo)[4,5-b:4',5' -d]pyran-3a-yl)methyl (2R,4S)-3-(4-methoxyphenyl)-4-phenylthiazolidine-2carboxylate (3w). Purified by flash column chromatography (silica gel, PE/EA = 64/1 to 16/1 as eluent). White solid, 56% yield, 14:11 dr. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.33-7.10 (m, 5H), 6.75-6.58 (m, 2H), 6.46-6.35 (m, 2H), 5.35 (d, J = 4.1 Hz, 1H), 5.25-5.20 (m, 2H), 4.33-4.16 (m, 1H), 4.35-4.14 (m, 4H), 3.97-3.85 (m, 2H), 3.74 (dd, J = 13.0, 1.9 Hz, 1H), 3.63 (s, 3H), 2.85 (dd, J = 11.2, 1.6 Hz, 1H), 1.51 (d, J = 10.9 Hz, 3H), 1.46-1.39 (m, 4H), 1.35-1.28 (m, 4H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  171.1, 152.5, 142.3, 138.5, 128.7, 127.6, 126.5, 115.4, 115.1, 115.0, 114.9, 109.3, 109.0, 101.5, 70.9, 70.6, 70.2, 66.7, 66.0, 63.9, 61.5, 55.7, 39.3, 26.7, 26.1, 25.6, 24.3. HRMS (ESI) calcd for C<sub>29</sub>H<sub>36</sub>NO<sub>8</sub>S (M+H<sup>+</sup>) 558.2156, found 558.2158.



*Ethyl 4-phenyl-3-(o-tolyl)thiazolidine-2-carboxylate* (*3x*). Purified by flash column chromatography (silica gel, PE/EA = 64/1 to 16/1 as eluent). White solid, 40% yield, > 20:1 dr. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.36-7.27 (m, 2H), 7.27-7.06 (m, 5H), 6.96 (dtd, *J* = 18.4, 7.4, 1.7 Hz, 2H), 5.52 (dd, *J* = 8.6, 6.4 Hz, 1H), 5.27 (s, 1H), 4.21-3.99 (m, 2H), 3.58 (dd, *J* = 10.0, 6.4 Hz, 1H), 3.16 (dd, *J* = 10.0, 8.6 Hz, 1H), 2.40 (s, 3H), 1.20 (t, *J* = 7.1 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  171.4, 142.2, 140.0, 134.3, 130.7, 128.4, 127.6, 127.5, 125.8, 125.0, 124.6, 66.5, 64.3, 61.0, 38.9, 18.2, 14.0. HRMS (ESI) calcd for C<sub>19</sub>H<sub>21</sub>NO<sub>2</sub>S(M+Na<sup>+</sup>) 350.1185, found 350.1184.



*Ethyl (3-(4-methoxyphenyl)-4-phenylthiazolidine-2-carbonyl)glycinate (4a).* Purified by flash column chromatography (silica gel, PE/EA = 16/1 to 6/1 as eluent). White solid, 70% yield, > 20:1 dr. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.32-7.27 (m, 1H), 7.25-7.21 (m, 1H), 7.17-7.12 (m, 2H), 6.88 (dd, *J* = 6.7, 4.4 Hz, 1H), 6.73-6.67 (m, 2H), 6.54-6.48 (m, 2H), 5.47 (dd, *J* = 6.1, 1.5 Hz, 1H), 5.27 (s, 1H), 4.26-4.15 (m, 3H), 3.91-3.82 (m, 2H), 2.95 (dd, *J* = 11.3, 1.5 Hz, 1H), 1.26 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  171.9, 169.7, 152.9, 140.4, 137.9, 128.5, 127.7, 127.0, 116.2, 114.8, 66.9, 66.4, 61.7, 55.6, 41.4, 38.6, 14.2. HRMS (ESI) calcd for C<sub>21</sub>H<sub>25</sub>N<sub>2</sub>O<sub>4</sub>S (M+H<sup>+</sup>) 401.1530, found 401.1531.



*Methyl (3-(4-methoxyphenyl)-4-phenylthiazolidine-2-carbonyl)-L-alaninate (4b).* Purified by flash column chromatography (silica gel, PE/EA = 16/1 to 6/1 as eluent). White solid, 50% yield, 5:3 dr. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.31-7.26 (m, 2H), 7.26-7.21 (m, 1H), 7.15 (dt, *J* = 7.8, 1.8 Hz, 2H), 6.83 (d, *J* = 8.0 Hz, 1H), 6.77-6.64 (m, 2H), 6.56-6.46 (m, 2H), 5.50-5.43 (m, 1H), 5.23 (d, *J* = 2.0 Hz, 1H), 4.73-4.53 (m, 1H), 3.88-3.77 (m, 1H), 3.76 (s, 2H), 3.68 (d, *J* = 1.8 Hz, 3H), 3.66 (s, 1H), 2.95 (dd, *J* = 11.3, 1.7 Hz, 1H), 1.44 (d, *J* = 7.2 Hz, 1H), 1.31 (d, *J* = 7.2 Hz, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  173.5, 170.9, 153.0, 140.4, 137.9, 128.5, 127.7, 126.3, 116.3, 114.8, 66.9, 66.6, 55.6, 52.7, 48.1, 38.5, 18.5. HRMS (ESI) calcd for C<sub>21</sub>H<sub>25</sub>N<sub>2</sub>O<sub>4</sub>S (M+H<sup>+</sup>) 401.1530, found 401.1526.


*Methyl (3-(4-methoxyphenyl)-4-phenylthiazolidine-2-carbonyl)-L-valinate (4c).* Purified by flash column chromatography (silica gel, PE/EA = 16/1 to 6/1 as eluent). White solid, 70% yield, 1:1 dr. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.27-7.22 (m, 2H), 7.26-7.20 (m, 1H), 7.16-7.13 (m, 2H), 5.74-5.45 (m, 1H), 6.74-6.65 (m, 2H), 6.57-6.49 (m, 2H), 5.54-5.45 (m, 1H), 5.27 (d, *J* = 13.0 Hz, 1H), 4.72-4.53 (m, 1H), 3.92-3.76 (m, 1H), 3.75 (s, 2H), 3.68 (d, *J* = 1.8 Hz, 3H), 3.59 (s, 1H), 2.97-2.93 (m, 1H), 2.27-2.17 (m, 1H), 0.98-0.90 (m, 3H), 0.80-0.61 (m, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  172.6, 171.9, 171.8, 171.0, 153.02, 152.98, 140.5, 137.9, 137.8, 128.5, 127.7, 126.96, 126.95, 116.5, 116.2, 114.9, 114.8, 66.9, 66.7, 66.5, 57.1, 57.0, 55.7, 55.6, 52.4, 52.2, 38.7, 38.4, 31.7, 31.6, 29.8, 19.2, 19.1, 17.9, 17.3. HRMS (ESI) calcd for C<sub>23</sub>H<sub>29</sub>N<sub>2</sub>O<sub>4</sub>S (M+H<sup>+</sup>) 429.1843, found 429.1840.



*Methyl* (3-(4-methoxyphenyl)-4-phenylthiazolidine-2-carbonyl)-L-leucinate (4d). Purified by flash column chromatography (silica gel, PE/EA = 16/1 to 6/1 as eluent). White solid, 58% yield, 1:1 dr. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.30-7.19 (m, 4H), 7.16-7.10 (m, 2H), 6.70-6.65 (m, 2H), 6.52-6.47 (m, 2H), 5.49-5.42 (m, 1H), 5.23 (d, *J* = 8.1 Hz, 1H), 4.71-4.60 (m, 1H), 3.90-3.68 (m, 3H), 3.66 (s, 3H), 3.58 (s, 2H), 2.95-2.91 (m, 1H), 1.73-1.61 (m, 1H), 1.60-1.50 (m, 1H), 1.44-1.29 (m, 1H), 0.93 (dd, *J* = 6.0, 1.4 Hz, 3H), 0.84 (d, *J* = 6.4 Hz, 2H), 0.74 (d, *J* = 6.5 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  173.4, 172.7, 171.6, 171.0, 152.88, 152.86, 140.4, 140.3, 137.8, 137.7, 128.4, 127.60, 127.57, 126.9, 116.4, 116.1, 114.7, 114.6, 66.8, 66.7, 66.42, 66.37, 55.6, 55.5, 52.4, 52.2, 50.7, 50.5, 41.6, 41.5, 38.6, 38.4, 25.0, 24.6, 22.9, 22.8, 21.9, 21.6. HRMS (ESI) calcd for C<sub>24</sub>H<sub>31</sub>NO<sub>4</sub>S (M+H<sup>+</sup>) 443.1999, found 443.2004.



*Methyl* ((2*R*,4*R*)-3-(4-methoxyphenyl)-4-phenylthiazolidine-2-carbonyl)-Lmethioninate (4e). Purified by flash column chromatography (silica gel, PE/EA = 32/1 to 8/1 as eluent). White solid, 68% yield, 1:1 dr. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.31-7.22 (m, 3H), 7.17-7.14 (m, 2H), 6.75-6.66 (m, 2H), 6.56-6.47 (m, 2H), 5.49 (t, J = 5.6 Hz, 1H), 5.25 (d, J = 7.7 Hz, 1H), 4.82-4.62 (m, 1H), 3.93-3.78 (m, 1H), 3.76 (s, 1H), 3.68 (s, 3H), 3.65 (s, 2H), 2.98-2.94 (m, 1H), 2.59-2.44 (m, 1H), 2.30-2.21 (m, 1H), 2.14-1.98 (m, 3H), 1.97-1.82 (m, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  172.4, 171.9, 171.8, 171.2, 153.0, 140.5, 140.4, 137.9, 137.8, 128.5, 127.73, 127.70, 126.93, 126.92, 116.5, 116.0, 114.9, 114.8, 66.8, 66.7, 66.44, 66.35, 55.7, 55.6, 52.8, 52.6, 51.8, 51.6, 38.7, 38.5, 31.3, 31.0, 30.1, 29.7, 15.7, 15.2. HRMS (ESI) calcd for C<sub>23</sub>H<sub>29</sub>N<sub>2</sub>O<sub>4</sub>S<sub>2</sub> (M+H<sup>+</sup>) 461.1563, found 461.1568.



*Ethyl* 3-(4-(2-((*tert-butoxycarbonyl*)*amino*)-3-*methoxy*-3-*oxopropyl*)*phenyl*)-4*phenylthiazolidine-2-carboxylate* (4*f*). Purified by flash column chromatography (silica gel, PE/EA = 32 to 8/1 as eluent). White solid, 40% yield, > 20:1 dr. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.37-7.26 (m, 5H), 6.86 (dd, *J* = 8.3, 5.1 Hz, 2H), 6.39 (dd, *J* = 8.8, 2.2 Hz, 2H), 5.35 (d, *J* = 2.3 Hz, 1H), 5.28 (d, *J* = 7.0 Hz, 1H), 4.88 (t, *J* = 9.3 Hz, 1H), 4.46 (p, *J* = 6.7, 5.9 Hz, 1H), 4.32-4.16 (m, 2H), 3.99 (dd, *J* = 11.3, 7.1 Hz, 1H), 3.65 (d, *J* = 3.2 Hz, 3H), 2.89 (t, *J* = 9.5 Hz, 2H), 1.39 (s, 9H), 1.30-1.29 (m, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  172.8, 172.6, 171.7, 143.4, 142.3, 130.3, 128.7, 127.7, 126.4, 125.0, 113.7, 80.0, 65.9, 63.6, 61.8, 54.6, 52.3, 39.3, 29.8, 28.4, 14.3. HRMS (ESI) calcd for C<sub>27</sub>H<sub>35</sub>N<sub>2</sub>O<sub>6</sub>S (M+H<sup>+</sup>) 515.2210, found 515.2206.



*Ethyl* 4-(4-chlorophenyl)-3-(4-methoxyphenyl)thiazolidine-2-carboxylate (5a). Purified by flash column chromatography (silica gel, PE/EA = 64/1 to 16/1 as eluent). Yellow solid, 70% yield, > 20:1 dr. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.56 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.5 Hz, 2H), 6.75-6.68 (m, 2H), 6.52-6.44 (m, 2H), 5.12 (s, 1H), 5.00 (dd, *J* = 10.0, 5.6 Hz, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 3.69 (s, 3H), 3.43 (dd, *J* = 11.7, 10.0 Hz, 1H), 3.33 (dd, *J* = 11.7, 5.6 Hz, 1H), 1.37 (t, *J* = 7.1 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  172.4, 153.0, 140.1, 139.8, 133.5, 129.2, 128.2, 116.0, 114.6, 69.1, 67.3, 62.0, 55.7, 40.1, 14.3. HRMS (ESI) calcd for C<sub>19</sub>H<sub>21</sub>ClNO<sub>3</sub>S (M+H<sup>+</sup>) 378.0925, found 378.0922.



*Ethyl* (4-(4-chlorophenyl)-3-(4-methoxyphenyl)thiazolidine-2-carbonyl)glycinate (5b). Purified by flash column chromatography (silica gel, PE/EA = 32/1 to 8/1 as eluent). Yellow solid, 57% yield, > 20:1 dr. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.24 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 6.89-6.84 (m, 1H), 6.70 (d, *J* = 9.1 Hz, 2H), 6.48 (d, *J* = 9.1 Hz, 2H), 5.42 (d, *J* = 6.0 Hz, 1H), 5.25 (s, 1H), 4.25-4.11 (m, 3H), 3.90-3.82 (m, 2H), 3.67 (s, 3H), 2.89 (dd, *J* = 11.5, 1.4 Hz, 1H), 1.25 (t, *J* = 7.1 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  171.7, 169.8, 153.0, 139.0, 137.6, 133.5, 128.7, 128.4, 116.2, 114.9, 66.20, 66.19, 61.8, 55.6, 41.5, 38.5, 14.2. HRMS (ESI) calcd for C<sub>21</sub>H<sub>23</sub>ClN<sub>2</sub>O<sub>4</sub>SNa (M+Na<sup>+</sup>) 457.0959, found 457.0960.



*Ethyl* 4-(4-bromophenyl)-3-(4-methoxyphenyl)thiazolidine-2-carboxylate (5c). Purified by flash column chromatography (silica gel, PE/EA = 32/1 to 8/1 as eluent). Yellow solid, 69% yield, > 20:1 dr. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.49-7.41 (m, 2H), 7.25-7.17 (m, 2H), 6.76-6.68 (m, 2H), 6.48-6.39 (m, 2H), 5.36 (d, *J* = 1.2 Hz, 1H), 5.21 (d, *J* = 7.2 Hz, 1H), 4.30-4.13 (m, 2H), 3.96 (dd, *J* = 11.2, 7.2 Hz, 1H), 3.69 (d, *J* = 1.2 Hz, 3H), 2.85 (dd, *J* = 11.3, 1.6 Hz, 1H), 1.26-1.30 (m, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  171.6, 152.4, 141.7, 138.4, 131.8, 128.2, 121.4, 114.9, 65.4, 64.0, 61.8, 55.7, 39.1, 14.3. HRMS (ESI) calcd for C<sub>19</sub>H<sub>21</sub>BrNO<sub>3</sub>S (M+H<sup>+</sup>) 422.0420, found 422.0423.



*Ethyl* (4-(4-bromophenyl)-3-(4-methoxyphenyl)thiazolidine-2-carbonyl)glycinate (5d). Purified by flash column chromatography (silica gel, PE/EA = 32/1 to 8/1 as eluent). Yellow solid, 53% yield, > 20:1 dr. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.44-7.38 (m, 2H), 7.06-6.99 (m, 2H), 6.81 (dd, J = 6.7, 4.2 Hz, 1H), 6.73-6.68 (m, 2H), 6.52-6.44 (m, 2H), 5.41 (d, J = 5.9 Hz, 1H), 5.24 (s, 1H), 4.27-4.14 (m, 3H), 3.93-3.81 (m, 2H), 3.68 (s, 3H), 2.90 (dd, J = 11.5, 1.4 Hz, 1H), 1.25 (t, J = 7.2 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  171.6, 169.7, 153.0, 139.5, 137.6, 131.7, 128.7, 121.6, 116.2, 114.9, 66.24, 66.19, 61.8, 55.6, 41.4, 38.4, 14.2. HRMS (ESI) calcd for C<sub>21</sub>H<sub>24</sub>BrN<sub>2</sub>O<sub>4</sub>S (M+H<sup>+</sup>) 479.0635, found 479.0636.



*Ethyl* 4-([1,1'-biphenyl]-4-yl)-3-(4-methoxyphenyl)thiazolidine-2-carboxylate (5e). Purified by flash column chromatography (silica gel, PE/EA = 64/1 to 16/1 as eluent). Yellow solid, 87% yield, > 20:1 dr. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.57 (t, *J* = 7.8 Hz, 4H), 7.45-7.39 (q, *J* = 7.9 Hz, 4H), 7.37-7.31 (m, 1H), 6.75 (d, *J* = 9.0 Hz, 2H), 6.51 (d, *J* = 9.1 Hz, 2H), 5.42 (s, 1H), 5.32 (d, *J* = 7.0 Hz, 1H), 4.33-4.17 (m, 2H), 4.02 (dd, *J* = 11.2, 7.2 Hz, 1H), 3.70 (s, 3H), 2.95 (dd, *J* = 11.2, 1.5 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  171.8, 152.3, 141.6, 140.9, 140.5, 138.8, 128.9, 127.44, 127.37, 127.2, 126.9, 114.99, 114.96, 65.8, 64.1, 61.7, 55.7, 39.3, 14.3. HRMS (ESI) calcd for C<sub>25</sub>H<sub>26</sub>NO<sub>3</sub>S (M+H<sup>+</sup>) 420.1628, found 420.1630.



*Ethyl* (4-([1,1'-biphenyl]-4-yl)-3-(4-methoxyphenyl)thiazolidine-2-carbonyl) glycinate (5f). Purified by flash column chromatography (silica gel, PE/EA = 32/1 to 8/1 as eluent). Yellow solid, 52% yield, > 20:1 dr. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.58-7.48 (m, 4H), 7.45-7.38 (m, 2H), 7.37-7.29 (m, 1H), 7.21 (d, *J* = 8.3 Hz, 2H), 6.84 (dd, *J* = 6.7, 4.1 Hz, 1H), 6.76-6.70 (m, 2H), 6.59-6.52 (m, 2H), 5.53 (d, *J* = 5.8 Hz, 1H), 5.30 (s, 1H), 4.30-4.23 (m, 1H), 4.20 (q, *J* = 7.2 Hz, 2H), 3.95-3.82 (m, 2H), 3.69 (s, 3H), 3.00 (dd, *J* = 11.4, 1.4 Hz, 1H), 1.27 (t, *J* = 7.1 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  171.8, 169.8, 152.9, 140.7, 140.6, 139.3, 137.9, 128.9, 127.5, 127.4, 127.24, 127.15, 116.2, 114.9, 66.6, 66.4, 61.8, 55.6, 41.5, 38.7, 14.3. HRMS (ESI) calcd for C<sub>27</sub>H<sub>29</sub>N<sub>2</sub>O<sub>4</sub>S (M+H<sup>+</sup>) 477.1843, found 477.1848.



*Ethyl 3-(4-methoxyphenyl)-4-(p-tolyl)thiazolidine-2-carboxylate* (*5g*). Purified by flash column chromatography (silica gel, PE/EA = 64/1 to 16/1 as eluent). Colourless oil, 82% yield, > 20:1 dr. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.49 (d, *J* = 8.1 Hz, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 6.74-6.66 (m, 2H), 6.55-6.46 (m, 2H), 5.12 (s, 1H), 4.99 (dd, *J* = 10.1, 5.5 Hz, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 3.68 (s, 3H), 3.50-3.44 (m, 1H), 3.33 (dd, *J* = 11.7, 5.5 Hz, 1H), 2.31 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  172.5, 152.9, 140.6, 138.1, 137.5, 129.7, 126.7, 116.0, 114.6, 69.6, 67.4, 61.9, 55.7, 40.3, 21.3, 14.3. HRMS (ESI) calcd for C<sub>20</sub>H<sub>23</sub>NO<sub>3</sub>SNa (M+Na<sup>+</sup>) 380.1291, found 380.1292.



*Ethyl* (3-(4-methoxyphenyl)-4-(p-tolyl)thiazolidine-2-carbonyl)glycinate (5h). Purified by flash column chromatography (silica gel, PE/EA = 32/1 to 8/1 as eluent). White solid, 66% yield, > 20:1 dr. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.08 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 8.2 Hz, 2H), 6.89-6.85 (m, 1H), 6.73-6.67 (m, 2H), 6.55-6.48 (m, 2H), 5.44 (dd, *J* = 6.1, 1.4 Hz, 1H), 5.25 (s, 1H), 4.29-4.21 (m, 1H), 4.20-4.15 (m, 2H), 3.92-3.81 (m, 2H), 3.68 (s, 3H), 2.92 (dd, *J* = 11.4, 1.5 Hz, 1H), 2.30 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  171.9, 169.7, 152.9, 138.0, 137.4, 137.3, 129.2, 126.9, 116.3, 114.8, 66.7, 66.4, 61.7, 55.6, 41.5, 38.7, 21.2, 14.2. HRMS (ESI) calcd for C<sub>22</sub>H<sub>27</sub>N<sub>2</sub>O<sub>4</sub>S (M+H<sup>+</sup>) 415.1686, found 415.1691.



*Ethyl 3-(4-methoxyphenyl)-4-(m-tolyl)thiazolidine-2-carboxylate (5i).* Purified by flash column chromatography (silica gel, PE/EA = 64/1 to 16/1 as eluent). White solid, 85% yield, > 20:1 dr. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.38-7.26 (m, 2H), 7.21 (dd, *J* = 16.4, 7.6 Hz, 2H), 6.87-6.80 (m, 2H), 6.61-6.55 (m, 2H), 5.49 (s, 1H), 5.34 (dd, *J* = 7.3, 1.5 Hz, 1H), 4.42-4.27 (m, 2H), 4.08 (dd, *J* = 11.1, 7.2 Hz, 1H), 3.80 (s, 3H), 3.00 (dd, *J* = 11.2, 1.5 Hz, 1H), 2.45 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  171.9, 152.2, 142.6, 138.8, 138.3, 128.5, 128.4, 127.0, 123.6, 114.9, 66.0, 64.1, 61.6, 55.6, 39.3, 21.7, 14.3. HRMS (ESI) calcd for C<sub>20</sub>H<sub>24</sub>NO<sub>3</sub>S (M+H<sup>+</sup>) 358.1471, found 358.1472.



*Ethyl* (3-(4-methoxyphenyl)-4-(m-tolyl)thiazolidine-2-carbonyl)glycinate (5j). Purified by flash column chromatography (silica gel, PE/EA = 32/1 to 8/1 as eluent). White solid, 61% yield, > 20:1 dr. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.43 (t, J = 7.6 Hz, 1H), 7.33 (d, J = 7.6 Hz, 1H), 7.19 (d, J = 7.7 Hz, 1H), 7.13 (dd, J = 6.6, 4.3 Hz, 1H), 7.03-6.95 (m, 2H), 6.83-6.76 (m, 2H), 5.71 (d, J = 6.0 Hz, 1H), 5.55 (s, 1H), 4.59-4.41(m, 3H), 4.23-4.09 (m, 2H), 3.96 (s, 3H), 3.22 (dd, J = 11.4, 1.4 Hz, 1H), 2.59 (s, 3H), 1.54 (t, J = 7.2 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  172.0, 169.8, 152.8, 140.4, 138.1, 138.0, 128.5, 128.3, 127.5, 124.1, 116.1, 114.8, 66.8, 66.3, 61.7, 55.6, 41.5, 38.6,21.7, 14.2. HRMS (ESI) calcd for C<sub>22</sub>H<sub>27</sub>N<sub>2</sub>O<sub>4</sub>S (M+H<sup>+</sup>) 415.1686, found 415.1687.



*Ethyl* 4-(4-ethoxyphenyl)-3-(4-methoxyphenyl)thiazolidine-2-carboxylate (5k). Purified by flash column chromatography (silica gel, PE/EA = 64/1 to 16/1 as eluent). White solid, 82% yield, > 20:1 dr. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.22 (d, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 6.71 (d, *J* = 9.0 Hz, 2H), 6.45 (d, *J* = 9.0 Hz, 2H), 5.34 (s, 1H), 5.21 (dd, *J* = 7.1, 1.5 Hz, 1H), 4.27-4.15 (m, 2H), 4.02-3.90 (m, 3H), 3.68 (s, 3H), 2.86 (dd, *J* = 11.0, 1.6 Hz, 1H), 1.39 (t, *J* = 7.0 Hz, 3H), 1.27 (t, *J* = 7.1 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  171.9, 158.4, 152.2, 138.8, 134.3, 127.5, 115.0, 114.9, 114.6, 65.5, 64.0, 63.5, 61.7, 55.7, 39.5, 15.0, 14.3. HRMS (ESI) calcd for C<sub>21</sub>H<sub>26</sub>NO<sub>4</sub>S (M+H<sup>+</sup>) 388.1577, found 388.1582.



*Ethyl* 3-(4-methoxyphenyl)-4-(phenoxymethyl)thiazolidine-2-carboxylate (51). Purified by flash column chromatography (silica gel, PE/EA = 64/1 to 16/1 as eluent). White solid, 70% yield, 11:9 dr. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.27-7.20 (m, 2H), 7.08-6.48 (m, 7H), 5.11 (s, 1H), 4.29-4.07 (m, 3H), 4.06-3.85 (m, 4H), 3.71 (d, *J* = 6.6 Hz, 3H), 1.70-1.25 (m, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  171.8, 158.5, 153.9, 141.1, 129.7, 121.3, 116.9, 114.9, 114.7, 70.2, 65.4, 61.7, 55.7, 53.7, 46.0, 14.2. HRMS (ESI) calcd for  $C_{20}H_{24}NO_4S$  (M+H<sup>+</sup>) 374.1421, found 374.1420.



*Ethyl* 4-(*methoxymethyl*)-3-(4-*methoxyphenyl*)*thiazolidine-2-carboxylate* (5*m*). Purified by flash column chromatography (silica gel, PE/EA = 64/1 to 16/1 as eluent). Colourless oil, 68% yield, 1:1 dr. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.87-6.79 (m, 2H), 6.76-6.66 (m, 2H), 5.18 (d, *J* = 40.3 Hz, 1H), 4.27-4.11 (m, 2H), 3.96-3.86 (m, 1H), 3.85-3.78 (m, 1H), 3.76 (t, *J* = 2.0 Hz, 3H), 3.73-3.64 (m, 1H), 3.61-3.40 (m, 2H), 3.37 (d, *J* = 7.1 Hz, 3H), 1.27-1.21 (m, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  172.0, 171.7, 153.8, 153.0, 141.2, 140.7, 117.0, 115.3, 115.0, 114.9, 74.6, 65.2, 63.3, 61.7, 61.6, 59.2, 59.1, 56.7, 55.8, 55.7, 53.9, 46.5, 45.7, 14.2. HRMS (ESI) calcd for C<sub>15</sub>H<sub>22</sub>NO<sub>4</sub>S (M+H<sup>+</sup>) 312.1264, found 312.1260.



*Ethyl* 4-((4-allyl-2-methoxyphenoxy)methyl)-3-(4-methoxyphenyl)thiazolidine-2carboxylate (5n). Purified by flash column chromatography (silica gel, PE/EA = 64/1 to 16/1 as eluent). White solid, 75% yield, 1:1 dr. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.89-6.78 (m, 3H), 6.76-6.67 (m, 4H), 6.02-5.88 (m, 1H), 5.31-5.13 (m, 1H), 5.12-5.04 (m, 2H), 4.27-3.90 (m, 7H), 3.85 (d, J = 3.7 Hz, 3H), 3.75 (d, J = 5.1 Hz, 3H), 3.33 (dd, J= 6.7, 1.7 Hz, 2H), 1.24 (dt, J = 17.4, 7.1 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$ 171.9, 171.5, 153.8, 153.1, 149.9, 149.8, 146.4, 146.2, 141.2, 140.6, 137.7, 137.6, 134.3, 134.1, 120.73, 120.68, 116.8, 115.84, 115.80, 115.78, 115.4, 115.1, 114.92, 114.88, 112.7, 72.1, 71.8, 65.3, 63.1, 61.7, 61.5, 56.9, 56.0, 55.9, 55.7, 53.7, 45.9, 45.4, 39.9, 14.18, 14.16. HRMS (ESI) calcd for C<sub>24</sub>H<sub>30</sub>NO<sub>5</sub>S (M+H<sup>+</sup>) 444.1839, found 444.1835.



*Ethyl 3-(4-methoxyphenyl)thiazolidine-2-carboxylate (50).* Purified by flash column chromatography (silica gel, PE/EA = 64/1 to 16/1 as eluent). Colourless oil, 78% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.86-6.79 (m, 2H), 6.74-6.67 (m, 2H), 5.13 (s, 1H), 4.26-4.14 (m, 2H), 3.85-3.75 (m, 2H), 3.75 (s, 3H), 3.61-3.30 (m, 1H), 3.10-3.04 (m, 1H), 1.27 (t, *J* = 7.1 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  171.8, 153.4, 141.0, 116.1, 114.9, 64.9, 61.6, 55.8, 53.7, 30.6, 14.2. HRMS (ESI) calcd for C<sub>13</sub>H<sub>18</sub>NO<sub>3</sub>S (M+H<sup>+</sup>) 268.1002, found 268.1000.



*Ethyl (3-(4-methoxyphenyl)thiazolidine-2-carbonyl)glycinate (5p).* Purified by flash column chromatography (silica gel, PE/EA = 32/1 to 8/1 as eluent). Yellow oil, 61% yield, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.35-7.27 (m, 1H), 6.96-6.72 (m, 4H), 4.98 (s, 1H), 4.21-4.12 (m, 3H), 3.97 (dd, *J* = 18.3, 5.0 Hz, 1H), 3.84-3.78 (m, 1H), 3.77 (d, *J* = 8.6 Hz, 3H), 3.68-3.62 (m, 1H), 3.36-3.19 (m, 1H), 2.99-3.04 (m, 1H), 1.26 (t, *J* = 7.3 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  172.0, 169.7, 154.5, 141.5, 117.4, 114.9, 69.2, 61.7, 55.73, 55.68, 41.4, 30.7, 14.2. HRMS (ESI) calcd for C<sub>15</sub>H<sub>21</sub>N<sub>2</sub>O<sub>4</sub>S (M+H<sup>+</sup>) 325.1217, found 325.1218.



*Methyl (3-(4-methoxyphenyl)thiazolidine-2-carbonyl)-L-leucinate (5q).* Purified by flash column chromatography (silica gel, PE/EA = 32/1 to 8/1 as eluent). Yellow oil,

57% yield, 1:1 dr. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.13 (dd, J = 9.1, 4.3 Hz, 1H), 6.82 (d, J = 15.8 Hz, 4H), 4.95 (d, J = 15.3 Hz, 1H), 4.61-4.72 (m, 1H), 3.77 (t, J = 1.4 Hz, 3H), 3.73 (s, 1H), 3.68 (s, 3H), 3.15-3.31 (m, 1H), 2.98-3.06 (m, 1H), 1.78-1.43 (m, 4H), 0.95 (dd, J = 6.3, 2.4 Hz, 3H), 0.91 (d, J = 6.1 Hz, 2H), 0.85 (d, J = 6.1 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 173.5, 173.1, 171.8, 171.3, 154.6, 154.4, 141.6, 141.4, 117.6, 117.2, 114.9, 114.8, 69.4, 69.1, 55.8, 55.74, 55.69, 55.6, 52.5, 52.4, 50.8, 50.6, 41.7, 41.3, 30.8, 30.6, 25.2, 25.0, 23.03, 22.99, 22.0, 21.8. HRMS (ESI) calcd for C<sub>18</sub>H<sub>27</sub>N<sub>2</sub>O<sub>4</sub>S (M+H<sup>+</sup>) 367.1686, found 367.1690.



*Ethyl* (2*R*,4*S*)-3-(4-methoxyphenyl)-4-(o-tolyl)thiazolidine-2-carboxylate. (5*r*). Purified by flash column chromatography (silica gel, PE/EA = 64/1 to 16/1 as eluent). Light yellow solid, 75% yield, >20:1 dr. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.27-7.03 (m, 4H), 6.69 (d, *J* = 9.0 Hz, 2H), 6.34 (d, *J* = 9.1 Hz, 2H), 5.39 (d, *J* = 5.7 Hz, 2H), 4.23 (dd, *J* = 7.9, 7.1 Hz, 2H), 3.97 (dd, *J* = 11.0, 7.3 Hz, 1H), 3.67 (s, 3H), 2.81 (dd, *J* = 11.0, 1.5 Hz, 1H), 2.48 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H); <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  171.8, 152.1, 139.6, 138.6, 133.9, 130.7, 127.3, 126.5, 126.1, 114.9, 114.6, 64.1, 63.0, 61.6, 55.6, 37.5, 19.4, 14.2. HRMS (ESI) calcd for C<sub>20</sub>H<sub>23</sub>NO<sub>3</sub>S(M+Na<sup>+</sup>) 380.1291, found 380.1291.



*Ethyl 3-(4-methoxyphenyl)-4-phenylthiazolidine-2-carboxylate 1-oxide (8a)*. Purified by flash column chromatography (silica gel, PE/EA = 8/1 to 4/1 as eluent). White solid, 75 % yield, > 20:1 dr. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.61 (dd, *J* = 7.3, 1.7 Hz, 2H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.28 (d, *J* = 7.2 Hz, 1H), 6.76-6.68 (m, 2H), 6.67-6.62 (m, 2H), 5.75 (dd, *J* = 11.6, 4.9 Hz, 1H), 5.29 (s, 1H), 4.36 (q, *J* = 7.2 Hz, 2H), 3.68 (s, 3H), 3.61-3.56 (m, 1H), 3.15-3.08 (m, 1H), 1.39 (t, *J* = 7.1 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)

δ 168.0, 154.0, 140.3, 139.6, 129.3, 128.2, 126.8, 117.5, 114.7, 89.4, 65.8, 62.8, 58.6, 55.6, 14.3. HRMS (ESI) calcd for C<sub>19</sub>H<sub>22</sub>NO<sub>4</sub>S (M+H<sup>+</sup>) 360.1264, found 360.1264.



*3-(4-Methoxyphenyl)-4-phenylthiazolidin-2-yl)methanol* (*8b*). Purified by flash column chromatography (silica gel, PE/EA = 6/1 to 2/1 as eluent). White solid, 92 % yield, 4:1 dr. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.23-7.14 (m, 5H), 6.69-6.64 (m, 2H), 6.62-6.57 (m, 2H), 5.22 (dd, *J* = 7.3, 3.9 Hz, 1H), 5.08 (dd, *J* = 6.4, 3.3 Hz, 1H), 3.88 (dd, *J* = 11.6, 3.9 Hz, 1H), 3.63 (s, 3H), 3.62-3.52 (m, 2H), 2.87 (dd, *J* = 11.2, 3.3 Hz, 1H), 2.52 (s, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  152.6, 141.0, 138.3, 128.3, 127.4, 127.2, 117.9, 114.6, 69.1, 65.8, 63.2, 55.5, 37.6. HRMS (ESI) calcd for C<sub>17</sub>H<sub>20</sub>NO<sub>2</sub>S (M+H<sup>+</sup>) 302.1209, found 302.1211.



*3-(4-Methoxyphenyl)-4-phenylthiazolidin-2-yl)methyl 4-(bis(2-chloroethyl)amino) benzoate* (*8c*). Purified by flash column chromatography (silica gel, PE/EA = 8/1 to 4/1 as eluent). White solid, 82 % yield, 4:1 dr. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.90 (d, *J* = 8.9 Hz, 2H), 7.25-7.15 (m, 5H), 6.71 (d, *J* = 5.8 Hz, 2H), 6.65 (d, *J* = 8.8 Hz, 2H), 5.47 (dd, *J* = 7.9, 4.3 Hz, 1H), 5.17 (dd, *J* = 6.5, 2.8 Hz, 1H), 4.80-4.75 (m, 1H), 4.16 (dd, *J* = 11.3, 7.9 Hz, 1H), 3.79 (t, *J* = 7.0 Hz, 4H), 3.72 (dd, *J* = 11.4, 6.5 Hz, 1H), 3.66-3.62 (m, 7H), 2.94 (dd, *J* = 11.3, 2.8 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  166.4, 152.6, 149.9, 141.3, 138.4, 132.1, 128.4, 127.2, 126.0, 118.6, 117.9, 114.7, 110.9, 65.5, 65.1, 64.8, 55.6, 53.4, 40.2, 38.1. HRMS (ESI) calcd for C<sub>28</sub>H<sub>31</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>3</sub>S (M+H<sup>+</sup>) 545.1427, found 545.1431.



*1-Benzyl* 5-((3-(4-methoxyphenyl)-4-phenylthiazolidin-2-yl)methyl) ((benzyloxy) carbonyl)-D-glutamate (8d). Purified by flash column chromatography (silica gel, PE/EA = 6/1 to 2/1 as eluent). White solid, 76 % yield, 4:1 dr. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.41-7.30 (m, 12H), 7.25-7.18 (m, 3H), 6.76 (d, *J* = 2.1 Hz, 1H), 6.71-6.63 (m, 3H), 5.56 (dd, *J* = 22.1, 8.3 Hz, 1H), 5.35 (dd, *J* = 7.8, 4.6 Hz, 1H), 5.19 (s, 2H), 5.13 (d, *J* = 3.8 Hz, 2H), 4.60-4.54 (m, 1H), 4.52-4.46 (m, 1H), 4.02-3.96 (m, 1H), 3.67 (s, 3H), 2.88-2.93 (m, 1H), 2.52-2.20 (m, 3H), 2.05-1.91 (m, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  172.5, 171.7, 156.0, 152.6, 141.1, 138.2, 136.2, 135.2, 128.7, 128.59, 128.57, 128.5, 128.3, 128.24, 128.17, 127.4, 127.1, 125.9, 117.8, 114.6, 67.4, 67.2, 65.5, 65.0, 64.6, 55.5, 53.4, 37.9, 30.1, 27.6. HRMS (ESI) calcd for C<sub>37</sub>H<sub>39</sub>N<sub>2</sub>O<sub>7</sub>S (M+H<sup>+</sup>) 655.2472, found 655.2468.

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## 8. Copies of <sup>1</sup>H and <sup>13</sup>C NMR Spectra

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