# Practical, general, and systematic method for optical resolution of *gem*-dihalo- and monohalocyclopropanecarboxylic acids utilizing chiral 1,1'-binaphtholmonomethyl ethers: Application to the synthesis of three chiral pesticides†‡

Hiroaki Yasukochi,<sup>a</sup> Takayuki Atago,<sup>a</sup> Akihiro Tanaka,<sup>a</sup> Hidefumi Nakatsuji,<sup>a</sup> Eri Yoshida,<sup>b</sup> Akikazu Kakehi,<sup>b</sup> Yoshinori Nishii<sup>b</sup> and Yoo Tanabe<sup>\*a</sup>

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We performed an efficient practical and systematic optical resolution method for *gem*-dihalo- and monohalocyclopropanecarboxylic acids **1** and **5** utilizing chiral 1,1'-binaphthol monomethyl ether (*R*)-**2** as the key auxiliary. Direct esterification of **1** with (*R*)-**2** gave two 1*R*- and 1*S*-diastereomeric esters **3** with marked different  $R_f$  values, both of which were easily separated using simple column chromatography. Monodehalogenation of separated chiral esters **3** using *t*-BuMgCl and cat. Co(dppe)<sub>2</sub>Cl<sub>2</sub> gave two 1,2-*trans*- and 1,2-*cis*-diastereomers **4** with markedly different  $R_f$  values, both of which were easily hydrolyzed to the desired enantiopure acids **1** (>99%) and **5** (>99%), respectively, with recovery of (*R*)-**2**, both in good to excellent yields. Utilizing the present method, important chiral agrochemicals, carpropamid **6** and fencyclate **7**, were readily synthesized. Pyrethroid **9** with three asymmetric centers was efficiently synthesized in a much better yield compared with the reported method.

# Introduction

gem-Dihalocyclopropanecarboxylic acids 1, representative cyclopropane derivatives, comprise a number of useful synthetic intermediates in many fields of organic chemistry.<sup>1</sup> There are, however, only two methods for the preparation of optically active gem-dihalocyclopropanecarboxylic acids. One is optical resolution using chiral amines: dehydroabiethylamine,<sup>2</sup> cinchonidine,<sup>3</sup> and (S)-1-(1-naphthyl)ethylamine,<sup>3</sup> but the resolution efficiency is not high. The other is a biotransformation method utilizing *Rhodococcus* sp. AJ270,<sup>4</sup> which is efficient in yield with high enantiomeric excess, but is limited to the use of 3-phenyl-2,2dihalo(or dimethyl)cyclopropanes.

The crucial problem of these methods lies in the lack of substrate generality. As a part of our ongoing program of synthetic studies on the transformation of *gem*-dihalocyclopropanes,<sup>3,5</sup> we previously disclosed a chirality exchange benzannulation from  $sp^3$  chirality to axial chirality<sup>3</sup> and a synthesis of unique pyrethroids bearing three asymmetric centers (Scheme 1).<sup>6</sup> The investigation into this asymmetric version required a more practical protocol for obtaining enantiopure *gem*-dihalocyclopropanes. We present here

a highly general and efficient method for the optical resolution of various, not only *gem*-dihaloyclopropanecarboxylic acids **1**, but also related monohalocyclopropanecarboxylic acids **5**, utilizing easily accessible column chromatographic separation.



Pyrethroids with Three Asymmetric Centers

Scheme 1 Examples of the utility of chiral *gem*-dihalo- and monohalo-cyclopropanecarboxylic acids.

# **Results and discussion**

Chiral 1,1'-binaphthol derivatives are well-recognized chiral catalysts and auxiliaries for the production of various useful optically active compounds. Yamamoto and Ishihara's group developed a monomethyl ether of chiral 1,1'-binaphthol (R)-2 that was utilized for the SnCl<sub>4</sub>-mediated enantioselective protonation of

<sup>&</sup>lt;sup>a</sup>Department of Chemistry, School of Science and Technology, Kwansei Gakuin University, 2-1 Gakuen, Sanda, Hyogo 669-1337, Japan. E-mail: tanabe@kwansei.ac.jp; Fax: +81-795-65-9077; Tel: +81-795-65-8394 <sup>b</sup>Department of Chemistry, Faculty of Textile Science and Technology, Shinshu University, Ueda, Nagano 386-8567, Japan. E-mail: nishii@ giptc.shinshu-u.ac.jp; Fax: +81-268-21-5391; Tel: +81-268-51-5403 † Electronic supplementary information (ESI) available: Experimental data of known and new compounds. See DOI: 10.1039/b714614k ‡ CCDC reference number 646350. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b714614k

enol silyl ethers.<sup>7</sup> A convenient preparation of (R)-2 from (R)-1,1'-binaphthol and MeOH was reported utilizing the Mitsunobu reaction.<sup>8</sup>

#### (A) Optical resolution of gem-dihaloyclopropanecarboxylic acids 1

We utilized (R)-2 as the auxiliary for the present column chromatographic optical resolution of *gem*-dihaloyclopropanecarboxylic acids 1 as outlined in Scheme 2.



Scheme 2 Optical resolution procedure of *gem*-dihalocyclopropane-carboxylic acids 1.

An initial examination of TsCl–*N*-methylimidazole-mediated direct esterification<sup>9</sup> between  $(\pm)$ -2,2-dichloro-1-methylcyclopropanecarboxylic acid [ $(\pm)$ -1a] and (*R*)-2 resulted in the formation of diastereomeric mixtures of (1R)-3a and (1S)-3a, which displayed significantly different  $R_f$  values, 0.37 and 0.46, respectively, on a SiO<sub>2</sub>-thin-layer chromatography (hexane–AcOEt = 5 : 1). Thus, esters (1R)-3a and (1S)-3a were easily separated by SiO<sub>2</sub>-column chromatography in 39% and 41% yield, respectively.

This protocol showed high generality for various acids 1a-g in good yield (Table 1). The salient features are as follows. (i) All 7 examples examined had distinctively different  $R_f$  values between (1R)-3 and (1S)-3 diastereomers. (ii) Diastereomers (1S)-3a-g showed consistently higher  $R_f$  values compared with those of the corresponding diastereomers (1R)-3a-g. (iii) Important chiral acid precursors for the fungicide carpropamid<sup>10</sup> (1S,3R)-1e (entry 5) and the synthetic pyrethroid fencyclate<sup>11</sup> (1S)-1f (entry 6), were readily prepared (*vide infra*, Schemes 4 and 5). (iv) A gem-dibrominated analog 1g also produced good results (entry 7).

Separated diastereomers 3a-g and 3a'-g' were readily hydrolyzed under conventional conditions (KOH/THF-H<sub>2</sub>O, 60-65 °C) to give the desired chiral *gem*-dihaloyclopropanecarboxylic acids 1a-g and 1a'-g', respectively, which were isolated by a facile extraction



Scheme 3 Optical resolution procedure of monohalocyclopropanecarboxylic acids 5.

procedure in good to excellent yields. The obtained aqueous reaction phase was washed with ether, and then acidified with HCl aq., followed by re-extraction with AcOEt. The organic phase contained sufficiently pure products 1a-g and 1a'-g'. Note that chiral auxiliary (*R*)-2 was recovered in *ca.* 95% yield by the initial ether extraction. Table 2 lists these results.

The absolute configurations of **1** were unambiguously deduced by comparing with the corresponding known compounds for **1a**, **d**–**g**. That of new compound (1S,3S)-**1b** was determined by X-ray crystallographic analysis of the corresponding amide derived from (S)-1-phenylethylamine. (Fig. 1). The absolute configuration of diastereomeric acids (1R,3S)- and (1S,3R)-**1c** was deduced by analogy with the result of (1S,3S)-**1b**.



**Fig. 1** X-ray structure of (*S*)-1-phenylethylamide of (1*S*,3*S*)-1b (50% probability thermal ellipsoids).

## (B) Optical resolution of monohalocyclopropanecarboxylic acids 5

Next, we focused our attention on the optical resolution of three sets of analogous monohalocyclopropanecarboxylic acids **5** using a similar simple column chromatographic separation (Scheme 3). The ester precursors **4a–c** were prepared by reductive monodechlorination utilizing *t*-BuMgCl–cat. Co(dppe)<sub>2</sub>Cl<sub>2</sub> reduction<sup>12</sup> of the corresponding chiral 1,1'-binaphthol esters **3**. Table 3 lists these



 Table 1
 Optical resolution of gem-dihalocyclopropanecarboxylic acids  $(\pm)$ -1 utilizing chiral auxiliary (R)-2

 Table 2
 Hydrolysis of chiral gem-dihalocyclopropanecarboxylic esters 3

		CO2R* 1/ Th	KOH HF, H <sub>2</sub> O, 60 - 6:	<b>→</b> 5 °C	R <sup>2</sup> * *	$R^1$ $R^* =$	C C C C		
Entry	RCO <sub>2</sub> R* <b>3</b>	Product 1	Time/h	Yield (%) <sup>a</sup>	Entry	RCO <sub>2</sub> R* <b>3</b>	Product 1	Time/h	Yield (%) <sup>a</sup>
1	(1 <i>R</i> )- <b>3a</b>	(1 <i>R</i> )-1a	4.5	93	8	(1 <i>S</i> ,3 <i>R</i> )- <b>3d</b>	(1 <i>S</i> ,3 <i>R</i> )-1d	3.0	82
2	(1S)-3a	(1 <i>S</i> )-1a	4.5	96	9	(1 <i>R</i> ,3 <i>S</i> )-3e	(1R, 3S)-1e	2.5	94
3	(1 <i>R</i> ,3 <i>R</i> )- <b>3</b> b	(1R, 3R)-1b	15.0	92	10	(1S, 3R)-3e	(1S, 3R)-1e	2.5	95
4	(1 <i>S</i> ,3 <i>S</i> )- <b>3</b> b	(1S, 3S)-1b	15.0	92	11	(1 <i>R</i> )-3f	(1 <i>R</i> )-1f	7.0	98
5	(1R, 3S)-3c	(1R, 3S)-1c	5.0	89	12	(1 <i>S</i> )-3f	(1 <i>S</i> )-1f	7.0	94
6	(1S, 3R)-3c	(1S, 3R)-1c	5.0	88	13	(1 <i>R</i> )-3g	(1 <i>R</i> )-1g	6.5	89
7	(1 <i>R</i> ,3 <i>S</i> )- <b>3d</b>	(1 <i>R</i> ,3 <i>S</i> )-1d	4.5	87	14	(1 <i>S</i> )-3g	(1 <i>S</i> )-1g	7.0	93
<sup>a</sup> Isolated									

successful results. Notice that all six diastereomer pairs had distinctively different  $R_f$  values. 1,2-*trans* Diastereomers showed consistently higher  $R_f$  values, which was quite different from the result of the separation of esters **3**. Eventually, all 12 diastereomers

were produced in pure form (>99% de). KOH hydrolysis of 4a-c gave three sets of each of the four chiral acids 5a-c in good yield (Table 4). The purification procedure of all 4a-c (×4) was as convenient as the aforementioned case of acids 1.

R <sup>2</sup>	CO <sub>2</sub> R* <i>t</i> -BuMgCl cat. Co(dppe) <sub>2</sub> Cl <sub>2</sub> (0.05 eq	$\rightarrow$ $R^2 \star \star \star$	$CO_2R^*$ $R^2$	* CO <sub>2</sub> R* Me R* =	$\square$	
x	/ THF, 50 - 55 °C, 30 min	2R : *	2S		$\mathbf{C}$	Г <sup>\$</sup> )
3		<b>(2<i>R</i>)-4a - 0</b> > 99%	c (2S) % de	- <b>4a - c</b> \ > 99% de		/
Entry	Substrate	t-BuMgCl/eq.	Product	1,2-Configuration	$R_{ m f}{}^a$	Yield (%) <sup>b</sup>
1	$\sum_{CI} \sum_{CI} \sum_{CI} \sum_{(1R)-3a} \sum_{(1R)-3a} \sum_{i=1}^{N} \sum_{i=1}$	3.3	(1 <i>R</i> ,2 <i>R</i> )-4a (1 <i>R</i> ,2 <i>S</i> )-4a	1,2- <i>cis</i> 1,2- <i>trans</i>	0.52 0.65	19 51
2	Cl Cl (1 <i>S</i> )- <b>3a</b>	3.3	(1 <i>S</i> ,2 <i>R</i> )-4a (1 <i>S</i> ,2 <i>S</i> )-4a	1,2- <i>trans</i> 1,2- <i>cis</i>	0.60 0.46	46 24
3	Ph Me Cl $Cl$ $(1R,3S)$ -3b	4.0	(1 <i>R</i> ,2 <i>R</i> ,3S)- <b>4b</b> (1 <i>R</i> ,2 <i>S</i> ,3 <i>S</i> )- <b>4b</b>	1,2-cis 1,2-trans	0.62 0.66	40 38
4	Ph <sub>11</sub> , CO <sub>2</sub> R <sup>*</sup> Me CI CI (1 <i>S</i> ,3 <i>R</i> )- <b>3b</b>	4.0	(1 <i>S</i> ,2 <i>R</i> ,3 <i>R</i> )- <b>4b</b> (1 <i>S</i> ,2 <i>S</i> ,3 <i>R</i> )- <b>4b</b>	1,2- <i>trans</i> 1,2- <i>cis</i>	0.62 0.56	40 37
5	Br Br Br (1R)-3c	1.9	(1 <i>R</i> ,2 <i>R</i> )-4c (1 <i>R</i> ,2 <i>S</i> )-4c	1,2-cis 1,2-trans	0.56 0.69	35 42
6	Br Br (1.S)-3c	1.9	(1 <i>S</i> ,2 <i>R</i> )- <b>4</b> c (1 <i>S</i> ,2 <i>S</i> )- <b>4</b> c	1,2- <i>trans</i> 1,2- <i>cis</i>	0.45 0.33	40 33

 Table 3 Optical resolution of monohalocyclopropanecarboxylic esters 4a-c utilizing chiral auxiliary 2

<sup>*a*</sup> Hexane–AcOEt = 5:1. <sup>*b*</sup> Isolated.

Table 4	Hydrolysis of chiral	l monohalocyclopropane	ecarboxylic esters 5
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	R <sup>2</sup> * * CO <sub>2</sub> R* * Me X 4	КОН / THF - H <sub>2</sub> O - MeOH,	► 60 - 65 °C		CO <sub>2</sub> H 1e 5	CCC \$	
Entry	RCO <sub>2</sub> R* 4	Product 5	Yield (%) <sup>a</sup>	Entry	RCO <sub>2</sub> R* <b>4</b>	Product 5	Yield (%) <sup>a</sup>
1	(1 <i>R</i> ,2 <i>R</i> )- <b>4</b> a	(1 <i>R</i> ,2 <i>R</i> )-5a	92	7	(1 <i>S</i> ,2 <i>R</i> ,3 <i>R</i> )- <b>4</b> b	(1 <i>S</i> ,2 <i>R</i> ,3 <i>R</i> )- <b>5</b> b	93
2	(1R, 2S)-4a	(1R, 2S)-5a	95	8	(1S, 2S, 3R)-4b	(1S, 2S, 3R)-5b	92
3	(1S, 2R)-4a	(1S, 2R)-5a	92	9	(1R, 2R)-4c	(1R, 2R)-5c	97
4	(1S, 2S)-4a	(1S, 2S)-5a	92	10	(1R, 2S)-4c	(1R, 2S)-5c	94
5	(1R, 2R, 3S)-4b	(1R, 2R, 3S)-5b	93	11	(1S, 2R)-4c	(1S, 2R)-5c	92
6	(1 <i>R</i> ,2 <i>S</i> ,3 <i>S</i> )-4b	(1 <i>R</i> ,2 <i>S</i> ,3 <i>R</i> )- <b>5</b> b	92	12	(1S, 2S)-4c	(1 <i>S</i> ,2 <i>S</i> )-5c	96
" Isolated.							

## (C) Application to the synthesis of three pesticides

With these results in hand, we applied the present protocol to the synthesis of three chiral pesticides (Schemes 4 and 5). First, amide formation of acid (1S,3R)-1e with (S)-1-(4-chlorophenyl)ethylamine gave (1S,3R,1'S)-carpropamid 6, the most active ingredient among the stereoisomers, in good yield. The present method was more convenient, compared to the reported method<sup>6b</sup> using thin layer column chromatographic separation of diastereomers derived from  $(\pm)$ -4a and (S)-1-(4-chlorophenyl)ethylamine. Second, (1S)-fencyclate 7, a synthetic pyrethroid with a unique gemdichlorocyclopropane structure, was readily synthesized by the condensing acid (1S)-1f with 3-phenoxybenzyl(bromo)acetonitrile in good yield.



Scheme 4 Synthesis of chiral carpropamid 6 and fencyclate 7.



Scheme 5 Synthesis of pyrethroid with three asymmetric centers (1R, 2S, 3S)-9.

A monochlorocyclopropane pyrethroid with three asymmetric centers, (1R,2S,3S)-9, was efficiently synthesized (Scheme 5). LAH reduction of (1R,2S,3S)-5b gave alcohol (1R,2S,3S)-8 (95%), which was coupled with 3-phenoxybenzyl bromide to give the desired product (1R,2S,3S)-9 (84%). Our first synthesis of (1R,2S,3S)-9 required a tedious optical resolution step for the corresponding racemic acid  $(1R^*,2S^*,3S^*)$ -5b; four recrystallizations using (S)-naphthylethylamine resulted in a poor yield (3.5%) of 5b.<sup>6b</sup> Thus, total yield and efficiency were greatly increased up to *ca.* 40 times by the present method.

In conclusion, we developed an efficient general practical optical resolution method for *gem*-dihalo and monohalocyclo-propanecarboxylic acids using simple column chromatographic separation. The present systematic protocol was successfully applied to the short synthesis of three pesticides The use of equally available (S)-2 will also provide complementary antipodal *gem*-

dihalocyclopropanecarboxylic acids. Because of its high efficiency and generality, the present method provides a new avenue for the practical preparation of various cyclopropane derivatives. Further investigation, especially of new chirality exchange benzannulations utilizing the present method, is in progress.

# Experimental

Melting points were determined on a hot stage microscope apparatus (Yanagimoto) and are uncorrected. NMR spectra were recorded on a JEOL DELTA300 spectrometer, operating at 300 MHz for <sup>1</sup>H NMR and 75 MHz for <sup>13</sup>C NMR. Chemical shifts ( $\delta$  ppm) in CDCl<sub>3</sub> were reported downfield from TMS (= 0 ppm) for <sup>1</sup>H NMR. For <sup>13</sup>C NMR, chemical shifts on a scale relative to (77.00 ppm) as an internal reference. IR spectra were recorded on JASCO FT/IR-5300 spectrophotometer. Optical rotations were measured on a JASCO DIP-370 ( $\lambda$  589 nm). Mass spectra were measured on a JEOL JMS-T100LC spectrometer.

Data of known and new compounds: (1R,3R)-**3b**, (1S,3S)-**3b**, (1R,3S)-**3c**, (1S,3R)-**3c**, (1R,3S)-**3d**, (1S,3R)-**3d**, (1R,3S)-**3e**, (1S,3R)-**3e**, (1R)-**3f**, (1S)-**3f**, (1R)-**3g**, (1S)-**3g**, (1S)-**1a**, <sup>3</sup> (1R,3R)-**1b**, <sup>5b,c</sup> (1S,3S)-**1b**, <sup>5b,c</sup> (1R,3S)-**1c**, <sup>5b,c</sup> (1S,3R)-**1d**, <sup>6b</sup> (1R,3S)-**1e**, (1S,3R)-**1e**, (1R,3S)-**1e**, (1S,3R)-**1e**, (1R,3S)-**1e**, (1S,3R)-**1e**, (1R,3S)-**1e**, (1R,2R,3S)-**4b**, (1R,2S,3S)-**4b**, (1S,2R,3R)-**4b**, (1S,2S,3R)-**4b**, (1S,2R,3R)-**4b**, (1S,2S,3R)-**4b**, (1R,2R)-**4c**, (1R,2S)-**4c**, (1S,2R)-**4c**, (1S,2S)-**4c**, (1S,2R)-**4c**, (1S,2S)-**4c**, (1S,2R)-**5c**, (1S,2R)-**5c**, (1S,2R)-**5c**, (1S,2R)-**5c**, are described in the electronic supporting information.<sup>†</sup>

## A typical esterification procedure to give (1R)- and (1S)-[(R)-2'methoxy-1,1'-binaphth-2-yl] 2,2-dichloro-1-methylcyclopropanecarboxylate [(1R)-3a and (1S)-3a] (Table 1, entry 1)

TsCl (127 mg, 0.66 mmol) in CH<sub>3</sub>CN (0.60 ml) was added to a stirred solution of ( $\pm$ )-2,2-dichloro-1-methylcyclopropanecarboxylic acid [( $\pm$ )-**1a**; 112 mg, 0.66 mmol] and *N*-methylimidazole (136 mg, 1.66 mmol) in CH<sub>3</sub>CN (0.60 ml) at 0–5 °C under an Ar atmosphere, followed by being stirred at the same temp. for 0.5 h. (*R*)-Monomethyl ether of 1,1'-binaphthol (**2**; 166 mg, 0.55 mmol) in CH<sub>3</sub>CN (0.60 ml) was added to the reaction mixture at 0–5 °C, followed by being stirred at 20–25 °C for 2 h. Water was added to the mixture, which was extracted with AcOEt (5 ml × 3). The combined organic phase was washed with water, brine, dried (Na<sub>2</sub>SO<sub>4</sub>), and concentrated. The obtained crude product was purified by silica gel column chromatography (hexane–AcOEt = 15 : 1) to give the desired products (1*R*)-**3a** [99 mg, 39%; *R*<sub>f</sub> = 0.37 (hexane–AcOEt = 5 : 1)] and (1*S*)-**3a** [105 mg, 41%; *R*<sub>f</sub> = 0.46 (hexane–AcOEt = 5 : 1)].

(1*R*)-3a. Colorless crystals;  $R_f = 0.37$  (hexane–AcOEt = 5 : 1); mp 141–143 °C;  $[a]_D^{24}$  +99.0 (*c* 0.59, CHCl<sub>3</sub>). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  0.84 (3H, s), 1.17 (1H, d, *Jgem* = 7.6 Hz), 1.98 (1H, d, *Jgem* = 7.6 Hz), 3.73 (3H, s), 7.16 (1H, d, *J* = 8.3 Hz), 7.20–7.49 (7H, m), 7.83 (1H, d, *J* = 7.9 Hz), 7.88–8.02 (3H, m). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  17.3, 30.5, 35.3, 56.7, 62.1, 113.6, 117.4, 121.4, 123.7, 125.2, 125.6, 126.2, 126.5, 126.7, 127.8, 128.1, 128.9, 129.2, 130.1, 131.9, 133.6, 133.8, 146.5, 155.0, 167.2. IR (KBr) 1752, 1507, 1275, 1250, 1215, 1140, 1090, 818, 754 cm<sup>-1</sup>. HRMS (ESI) calcd for C<sub>26</sub>H<sub>20</sub>Cl<sub>2</sub>O<sub>3</sub> (M + Na<sup>+</sup>) 473.0687, found 473.0692. (1*S*)-3a. Colorless crystals;  $R_f = 0.46$  (hexane–AcOEt = 5 : 1); mp 74–76 °C;  $[a]_D^{24}$  –53.1 (*c* 0.66, CHCl<sub>3</sub>). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  0.82 (3H, s), 1.11 (1H, d, *Jgem* = 7.6 Hz), 1.93 (1H, d, *Jgem* = 7.6 Hz), 3.77 (3H, s), 7.12 (1H, d, *J* = 8.3 Hz), 7.17–7.34 (4H, m), 7.39–7.49 (3H, m), 7.83 (1H, d, *J* = 7.9 Hz), 7.93 (1H, d, *J* = 8.3 Hz), 7.96 (2H, d, *J* = 8.9 Hz). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  17.2, 30.5, 35.3, 56.6, 62.2, 113.4, 121.6, 123.7, 125.0, 125.2, 125.6, 126.1, 126.5, 126.7, 127.7, 128.2, 128.9, 129.1, 130.0, 131.9, 133.6, 133.7, 146.5, 154.9, 167.3. IR (KBr) 1755, 1508, 1273, 1252, 1215, 1146, 1084, 806 cm<sup>-1</sup>. HRMS (ESI) calcd for C<sub>26</sub>H<sub>20</sub>Cl<sub>2</sub>O<sub>3</sub> (M + Na<sup>+</sup>) 473.0687, found 473.0681.

## A typical hydrolysis procedure to give (1*R*)-2,2-dichloro-1-methylcyclopropanecarboxylic acid [(1*R*)-1a]<sup>3</sup> (Table 2, entry 1)

(1*R*)-**3a** (3.53 g, 7.82 mmol) and KOH (1.32 g, 23.5 mmol) in THF (36 ml), and H<sub>2</sub>O (22 ml) were heated with stirring at 60–65 °C for 4.5 h. After cooling down, water was added to the mixture, which was extracted twice with ether. The combined organic phase was washed with water, brine, dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated to give (*R*)-**2** (recovery, 2.25 g, 96%). Next, the separated aqueous phase was adjusted to pH 1 ~ pH 2 using aqueous 1 M HCl, and then re-extracted with ether twice. The separated organic phase was washed with water, brine, and dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated to give the desired product (1*R*)-**1a** (1.33 g, 93%).

Yellow oil :  $[a]_D^{25}$  +51.4 (*c* 1.77, CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  1.48 (1H, d, *Jgem* = 7.6 Hz), 1.16 (3H, s), 2.30 (1H, d, *Jgem* = 7.6 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  18.02, 31.18, 35.12, 62.61, 175.52. IR (neat) 3001, 1709, 1416, 1316, 945 cm<sup>-1</sup>.

# Preparation<sup>13</sup> of (1*S*,3*S*)-2,2-dichloro-1,3-dimethyl-*N*-[(*S*)-1-phenylethyl]cyclopropancarboxamide for X-ray analysis

(1*S*,3*S*)-2,2-Dichloro-1,3-dimethylcyclopropanecarbonyl chloride (129 mg, 0.64 mmol) prepared from acid (1*S*,3*S*)-**3b** was added to a stirred suspension of (*S*)-1-phenylethylamine (78 mg, 0.64 mmol), *N*-methylimidazole (5 mg, 0.06 mmol), TMEDA (7 mg, 0.06 mmol), and K<sub>2</sub>CO<sub>3</sub> (134 mg, 0.97 mmol) in CH<sub>3</sub>CN (0.5 mL) at 0–5 °C under an Ar atmosphere. The mixture was stirred at the same temperature for 1 h. Water was added to the mixture, which was extracted with AcOEt. The organic phase was washed with water, brine, dried (Na<sub>2</sub>SO<sub>4</sub>), and concentrated. The obtained crude product was purified by silica gel column chromatography (hexane–AcOEt = 6 : 1) to give the desired product (122 mg, 80%).

Colorless crystals; mp 104.0–105.0 °C;  $[a]_D^{23}$  –35.4 (*c* 0.42, CHCl<sub>3</sub>). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  1.34 (3H, d, *J* = 6.5 Hz), 1.49 (1H, t, *J* = 6.2), 1.51 (3H, d, *J* = 6.5), 1.58 (3H, s), 5.13 (1H, quint, *J* = 7.2), 5.89–5.73 (1H, br), 7.40–7.23 (5H, m). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  11.6, 21.5, 22.6, 35.3, 38.2, 49.0, 68.0, 126.1, 127.5, 128.8, 142.7, 166.9, IR (KBr) 3289, 3068, 2975, 2932, 1672, 1642, 1539, 1453 cm<sup>-1</sup>.

Data from the X-ray crystallographic analysis was deposited at Cambridge crystallographic data base centre (CCDC).<sup>‡</sup> OR-TEP drawing (50% probability thermal ellipsoids) is of (S)-1phenylethylamide of (1S,3S)-1b. There are two unsymmetrical molecules in this lattice and only of them is shown.

A colorless prismatic single crystal ( $0.68 \times 0.38 \times 0.06$  mm) grown from solvent was used for the unit-cell determinations and

data was collected by a Rigaku AFC5S four-circle diffractometer with graphite-monochromated Mo $K_a$  radiation ( $\lambda = 0.71069$  Å). Representative data is as follows:  $C_{14}H_{17}Cl_2NO$ ; M = 286.20; monoclinic, space group  $P2_1$  (#4), Z = 4 with a = 9.82 (3) Å, b =9.82 (3) Å, c = 16.09 (3) Å,  $\beta = 101.08$  (16)°, V = 1522.0 (66) Å<sup>3</sup> and  $D_{calc.} = 1.249g$  cm<sup>-3</sup>. All calculations were performed using the teXsan package.<sup>14</sup> The structure was solved by a direct method . The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were attached at the idealized position and not refined. The final R1 ( $I > 2.00\sigma(I)$ ), R all reflections, and  $_{w}R2$  all reflections factors after full-matrix least-squares refinements were 0.060, 0.228, and 0.214, respectively, for 3608 observed reflections, and the Flack parameter was -0.09 (16).

## Typical monodehalogenation procedure of *gem*-dihalocyclopropanecarboxylate (1*R*)-3a to give (1*R*,2*R*)- and (1*R*,2*S*)-[(*R*)-2'methoxy-1,1'-binaphth-2-yl]2-chloro-1-methylcyclopropanecarboxylate [(1*R*,2*R*)-4a and (1*R*,2*S*)-4a] (Table 3, entry 1)

*t*-BuMgCl (1.0 M in THF, 2.94 ml, 2.94 mmol) was added to a stirred mixture of (1*R*)-**3a** (400 mg, 0.89 mmol) and  $\text{CoCl}_2(\text{dppe})_2$  (23 mg, 0.04 mmol) in THF (2.0 ml) at 50–55 °C under an Ar atmosphere, followed by stirring at the same temp. for 0.5 h. Water was added to the mixture, which was extracted with AcOEt (5 ml × 3). The combined organic phase was washed with water, brine, dried (Na<sub>2</sub>SO<sub>4</sub>), and concentrated. The obtained crude product was purified by silica gel column chromatography (hexane–AcOEt = 15 :1) to give the desired product (1*R*,2*R*)-**4a** (70 mg, 19%) and (1*R*,2*S*)-**4a** (189 mg, 51%).

(1*R*,2*R*)-4a. Pale yellow crystals;  $R_f = 0.52$  (hexane–AcOEt = 5 : 1); mp 58–60 °C;  $[a]_D^{23}$  +36.9 (*c* 0.35, CHCl<sub>3</sub>). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  0.70 (3H, s), 0.91 (1H, t, J = 7.2 Hz), 1.47 (1H, dd, J = 5.2, 7.2 Hz), 2.84 (1H, dd, J = 5.2, 7.2 Hz), 3.75 (3H, s), 7.15 (1H, d, J = 8.3 Hz), 7.20–7.37 (4H, m), 7.39–7.52 (3H, m), 7.84 (1H, d, J = 8.3 Hz), 7.90–8.04 (3H, m). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  18.7, 22.0, 27.2, 38.5, 56.7, 113.6, 117.7, 121.9, 123.6, 125.0, 125.4, 125.4, 126.1, 126.4, 126.5, 127.7, 128.1, 129.0, 129.9, 131.7, 133.6, 133.8, 146.8, 155.0, 168.4. IR (KBr) 3484, 3059, 3005, 2965, 2936, 2839, 1752, 1622, 1593, 1508, 1318, 1138, 1084, 808, 747 cm<sup>-1</sup>. HRMS (ESI) calcd for C<sub>26</sub>H<sub>21</sub>ClO<sub>3</sub> (M + Na<sup>+</sup>) 439.1077, found 439.1073.

(1*R*,2*S*)-4a. Pale yellow crystals;  $R_f = 0.65$  (hexane–AcOEt = 5 : 1); mp 55–56 °C;  $[a]_D^{23}$  +46.3 (*c* 3.15, CHCl<sub>3</sub>). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  0.60 (1H, t, J = 5.2 Hz), 1.10 (3H, s), 1.20 (1H, dd, J = 5.2, 7.9 Hz), 2.70 (1H, dd, J = 5.2, 7.9 Hz), 3.76 (3H, s), 7.05 (1H, d, J = 8.3 Hz), 7.19–7.39 (4H, m), 7.40–7.50 (3H, m), 7.85–8.06 (4H, m). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  14.3, 24.0, 24.4, 39.4, 56.4, 113.2, 117.1, 121.6, 123.7, 124.9, 125.1, 125.5, 126.1, 126.4, 126.6, 127.9, 128.1, 128.8, 129.0, 130.2, 131.7, 133.4, 133.5, 146.8, 155.0, 168.4. IR (KBr) 3449, 3059, 2938, 2839, 1746, 1622, 1593, 1508, 1319, 1138, 1086, 810, 748 cm<sup>-1</sup>. HRMS (ESI) calcd for C<sub>26</sub>H<sub>21</sub>ClO<sub>3</sub> (M + Na<sup>+</sup>) 439.1077, found 439.1078.

## Typical hydrolysis procedure to give (1R,2R)-2-chloro-1-methylcyclopropanecarboxylic acid [(1R,2R)-5a] (Table 4, entry 1)

A mixture of (1R,2R)-4a (60 mg, 0.14 mmol), KOH (24 mg, 0.43 mmol) in water (0.20 ml), THF (1.0 ml), and MeOH (0.10 ml)

was heated with stirring at 60–65 °C for 2 h. After cooling down, water was added to the mixture, which was extracted twice with ether (5 ml × 3). The combined organic phase was washed with water, brine, dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated to give (*R*)-**2** (recovery, 40 mg, 95%). Next, the separated aqueous layer was adjusted to pH 1 ~ 2 using 6 M aqueous HCl solution, and was re-extracted with AcOEt (5 ml × 3). The combined organic phase was washed with water, brine, dried (Na<sub>2</sub>SO<sub>4</sub>), and concentrated to give the desired product (1*R*,2*R*)-**5a** (17 mg, 92%).

Pale yellow oil;  $[a]_{D}^{23}$  –29.7 (*c* 0.55, CHCl<sub>3</sub>). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  1.24 (1H, t, *J* = 6.9 Hz), 1.38 (3H, s), 1.81 (1H, dd, *J* = 5.5, 6.9 Hz), 3.13 (1H, dd, *J* = 5.5, 6.9 Hz). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  19.3, 23.1, 26.9, 39.5, 177.1. IR (KBr) 2928, 2731, 2617, 1699, 1466, 1422, 1329, 1238, 1209, 941, 909 cm<sup>-1</sup>. Anal. Calcd for C<sub>3</sub>H<sub>7</sub>ClO<sub>2</sub>; C, 44.63; H, 5.24, found: C, 44.3; H, 4.9%.

# Synthesis of (1S, 3R, 1'S)-carpropamid 6, the most fungicidally active stereoisomer

TsCl (243 mg, 1.27 mmol) in CH<sub>3</sub>CN (1.0 mL) was added to a stirred solution of (1S,3R)-1e (209 mg, 1.06 mmol) and *N*methylimidazole (241 mg, 3.18 mmol) in CH<sub>3</sub>CN (1.0 mL) at 0–5 °C under an Ar atmosphere, and the mixture was stirred for 30 min. (*S*)-1-(4-Chlorophenyl)ethylamine (165 mg, 1.06 mmol) in CH<sub>3</sub>CN (1.0 mL) was added to the stirred mixture at 0–5 °C, followed by being stirred at the same temp. for 2 h. Water was added to the stirred mixture, which was extracted with ether. The organic phase was washed with water, brine, dried (Na<sub>2</sub>SO<sub>4</sub>), and concentrated. The obtained crude product was purified by silica gel column chromatography (hexane–AcOEt = 10 : 1) to give the desired product (1*S*,3*R*,1'*S*)-6 (205 mg, 57%).

Colorless crystals; mp 169.0–169.5 °C;  $[a]_D^{23}$  +90.7 (*c* 1.00, MeOH). [lit.<sup>10c</sup> [*a*]\_D +87.9 (MeOH)] <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  0.99 (3H, t, J = 7.2 Hz), 1.20 (3H, d, J = 6.5 Hz), 1.53 (3H, d, J = 6.9 Hz), 1.48–1.61 (1H, m), 1.95 (1H, dt, J = 7.2 Hz), 2.21 (1H, q, J = 6.5 Hz), 5.17 (1H, quint, J = 7.2 Hz), 5.87–5.93 (1H, br), 7.30 (4H, m). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  8.6, 10.9, 21.2, 22.1, 29.7, 43.2, 48.8, 66.6, 127.9, 128.7, 141.0, 167.2, IR (KBr) 3270, 3057, 2878, 1644, 1530, 1493, 1456, 1414 cm<sup>-1</sup> These spectroscopic data completely matched with the reported data.<sup>10c</sup>

#### Synthesis of (1S)-fencyclate 7

Et<sub>3</sub>N (41 mg, 0.406 mmol) was added to a stirred mixture of (1*S*)- **1f** (88 mg, 0.340 mmol) and bromo(3-phenoxyphenyl)acetonitrile (117 mg, 0.406 mmol) in acetone (0.7 mL) at 0–5 °C, and the mixture was stirred at room temperature for 2 h. Aqueous 1 M HCl solution was added to the mixture, which was extracted with ether. The organic phase was washed with water, brine, dried (Na<sub>2</sub>SO<sub>4</sub>), and concentrated. The crude oil was subjected to silica gel column chromatography (hexane–AcOEt = 10 : 1) to give the desired product (134 mg, 82%).

Light yellow oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  1.40 (3H, q, J = 6.88), 2.079 (1H × 1/2, d, J = 7.91), 2.084 (1H × 1/2, d J = 7.91), 2.61 (1H × 1/2, d, J = 7.91), 2.62 (1H × 1/2, d J = 7.91), 3.92–4.08 (2H, m), 6.29 (1H × 1/2, s), 6.32 (1H × 1/2, s), 6.78–6.91 (2H, m), 6.91–7.44 (11H, m). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  30.7, 30.8, 43.79, 43.84, 61.5, 61.6, 63.5, 63.78, 63.83, 114.3,

114.4, 115.1, 115.2, 117.4, 117.5, 119.2, 119.4, 120.30, 120.35, 121.8, 122.3, 124.0, 124.1, 124.5, 124.6, 129.9, 130.0, 130.5, 130.6, 131.9, 132.7, 132.9, 156.2, 156.3, 158.0, 158.2, 159.4, 166.1

# (1*R*,2*S*,3*S*)-2-Chloro-1-methyl-3-phenylcyclopropylmethanol [(1*R*,2*S*,3*S*)-8]<sup>66</sup>

Compound (1R,2S,3S)-5 (50 mg, 0.10 mmol) in THF was added to a stirred suspension of LiAlH<sub>4</sub> (2 mg, 0.05 mmol) in THF at 0–5 °C and the mixture was stirred at room temperature for 2 h. Water was added to the mixture, which was extracted twice with Et<sub>2</sub>O. The combined organic phase was washed with water, brine, dried (Na<sub>2</sub>SO<sub>4</sub>), and concentrated. The obtained crude product was purified by silica gel column chromatography (hexane–AcOEt = 6 :1) to give the desired product (1*R*,2*S*,3*S*)-8 (19 mg, 95%).

Colorless oil;  $[a]_D{}^{23}$  –74.6 (*c* 0.70, CHCl<sub>3</sub>). [lit.<sup>66</sup>  $[a]_D{}^{23}$  –82.3 (*c* 1.31, CHCl<sub>3</sub>)]. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  1.13 (3H, s), 1.53 (1H, s), 2.28 (1H, d, *J* = 7.9 Hz), 3.45 (1H, d, *J* = 7.9 Hz), 3.57–3.71 (2H, m), 7.20–7.37 (5H, m). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  13.2, 27.8, 27.9, 41.0, 69.7, 126.6, 128.1, 131.0, 134.2. IR (neat) 3432, 3399, 3318, 3272, 2926, 2872, 1447, 1032, 725, 700 cm<sup>-1</sup>.

## (1R,2S,3S)-2-Chloro-1-methyl-3-phenylcyclopropylmethyl 3-phenoxybenzyl ether [(1R,2S,3S)-9],<sup>66</sup> a pyrethroid with three asymmetric centers

A mixture of (1R,2S,3S)-8 (15 mg, 0.08 mmol) and 3phenoxybenzyl bromide (20 mg, 0.08 mmol) in DMF was added to a stirred suspension of NaH (2 mg, 0.08 mmol) in DMF at 0–5 °C, followed by stirring at room temperature for 4 h. Water was added to the mixture, which was extracted twice with Et<sub>2</sub>O. The combined organic phase was washed with water, brine, dried (Na<sub>2</sub>SO<sub>4</sub>), and concentrated. The obtained crude product was purified by silica gel column chromatography (hexane–AcOEt = 50 :1) to give the desired product (1*R*,2*S*,3*S*)-9 (24 mg, 84%).

Colorless oil;  $[a]_D^{23}$  –47.2 (*c* 0.50, CHCl<sub>3</sub>). [lit.<sup>66</sup>  $[a]_D^{23}$  –48.3 (*c* 1.55, CHCl<sub>3</sub>)]. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  1.10 (3H, s), 2.27 (1H, d, *J* = 7.9 Hz), 3.43 (1H, d, *J* = 7.9 Hz), 3.48 (2H, s), 4.47–4.59 (2H, m), 6.90–7.17 (6H, m), 7.20–7.40 (8H, m). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  13.6, 25.9, 27.8, 29.7, 41.3, 72.3, 76.3, 117.5, 117.8, 119.1, 122.0, 123.4, 126.5, 128.0, 129.7, 131.0, 134.4, 140.3, 156.9, 157.6.

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