# 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†‡

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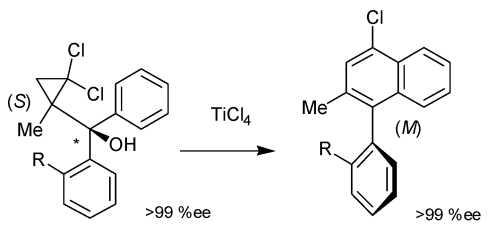
We performed an efficient practical and systematic optical resolution method for *gem*-dihalo- and monohalocyclopropanecarboxylic acids **1** and **5** utilizing chiral 1,1′-binaphthol monomethyl ether (*R*)-**2** as the key auxiliary. Direct esterification of **1** with (*R*)-**2** gave two 1*R*- and 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. $Co(dppe)_2Cl_2$ gave two 1,2-*trans*- and 1,2-*cis*-diastereomers **4** with markedly different $R_f$ values, both of which were similarly separated using simple column chromatography. The obtained diastereomers **3** and **4** 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.

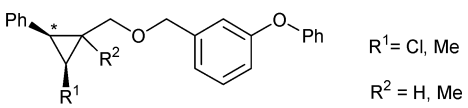
## Introduction

*gem*-Dihalocyclopropanecarboxylic acids **1**, representative cyclopropane derivatives, comprise a number of useful synthetic intermediates in many fields of organic chemistry.[1] There are, however, only two methods for the preparation of optically active *gem*-dihalocyclopropanecarboxylic acids. One is optical resolution using chiral amines: dehydroabiethylamine,[2] cinchonidine,[3] and (*S*)-1-(1-naphthyl)ethylamine,[3] but the resolution efficiency is not high. The other is a biotransformation method utilizing *Rhodococcus* sp. AJ270,[4] which is efficient in yield with high enantiomeric excess, but is limited to the use of 3-phenyl-2,2-dihalo(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,[3,5] we previously disclosed a chirality exchange benzannulation from $sp^3$ chirality to axial chirality[3] and a synthesis of unique pyrethroids bearing three asymmetric centers (Scheme 1).[6] 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.




***Chirality Exchange***




***Pyrethroids with Three Asymmetric Centers***

**Scheme 1** Examples of the utility of chiral *gem*-dihalo- and monohalocyclopropanecarboxylic 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 $SnCl_4$-mediated enantioselective protonation of

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[b]*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

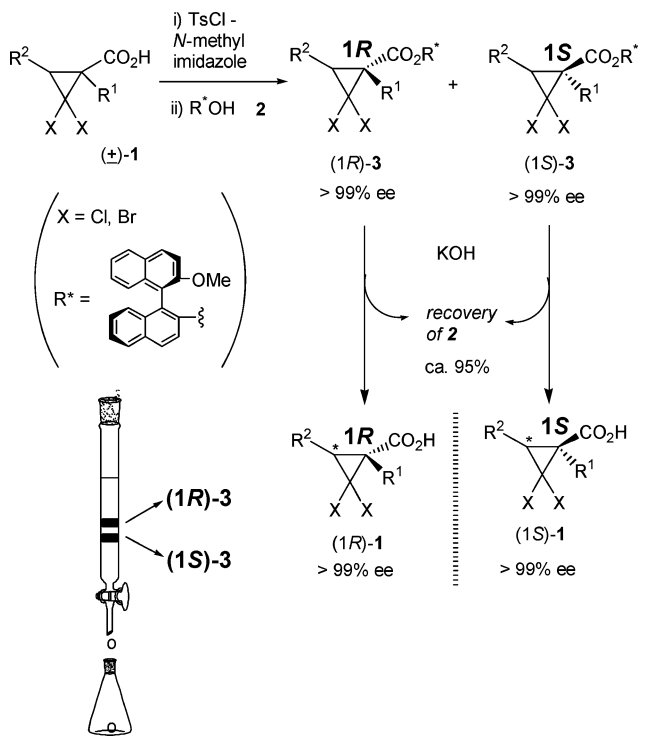
‡ CCDC reference number 646350. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b714614k

enol silyl ethers.[7] A convenient preparation of (*R*)-**2** from (*R*)-1,1′-binaphthol and MeOH was reported utilizing the Mitsunobu reaction.[8]

### (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.

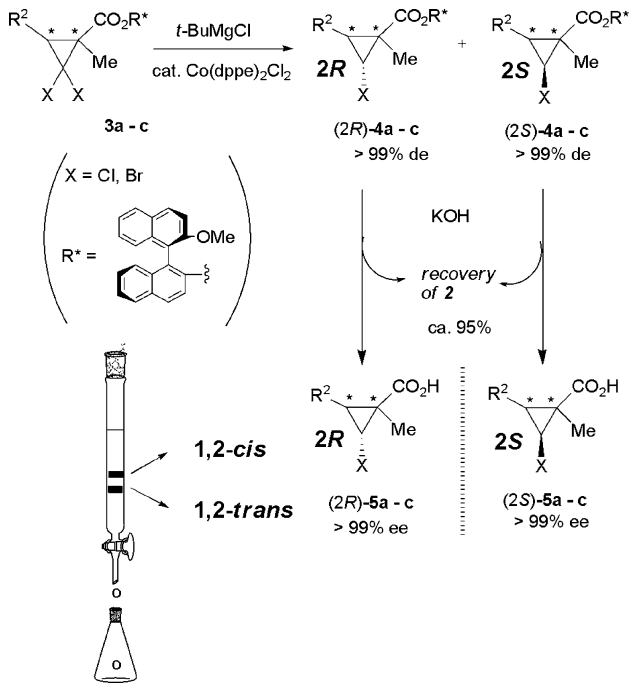



**Scheme 2** Optical resolution procedure of *gem*-dihalocyclopropanecarboxylic acids **1**.

An initial examination of TsCl–*N*-methylimidazole-mediated direct esterification[9] between (±)-2,2-dichloro-1-methylcyclopropanecarboxylic acid [(±)-**1a**] and (*R*)-**2** resulted in the formation of diastereomeric mixtures of (1*R*)-**3a** and (1*S*)-**3a**, which displayed significantly different $R_f$ values, 0.37 and 0.46, respectively, on a $SiO_2$-thin-layer chromatography (hexane–AcOEt = 5 : 1). Thus, esters (1*R*)-**3a** and (1*S*)-**3a** were easily separated by $SiO_2$-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 (1*R*)-**3** and (1*S*)-**3** diastereomers. (ii) Diastereomers (1*S*)-**3a–g** showed consistently higher $R_f$ values compared with those of the corresponding diastereomers (1*R*)-**3a–g**. (iii) Important chiral acid precursors for the fungicide carpropamid[10] (1*S*,3*R*)-**1e** (entry 5) and the synthetic pyrethroid fencyclate[11] (1*S*)-**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–$H_2O$, 60–65 °C) to give the desired chiral *gem*-dihaloyclopropanecarboxylic acids **1a–g** and **1a′–g′**, respectively, which were isolated by a facile extraction 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.




**Scheme 3** Optical resolution procedure of monohalocyclopropanecarboxylic acids **5**.

The absolute configurations of **1** were unambiguously deduced by comparing with the corresponding known compounds for **1a**, **d–g**. That of new compound (1*S*,3*S*)-**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 (1*R*,3*S*)- and (1*S*,3*R*)-**1c** was deduced by analogy with the result of (1*S*,3*S*)-**1b**.

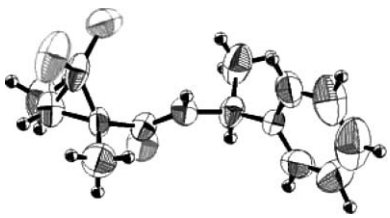
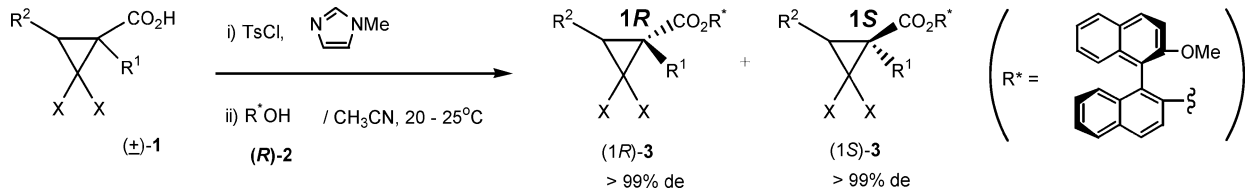


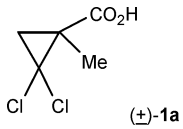
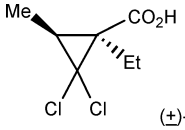
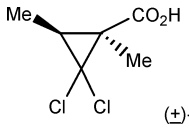
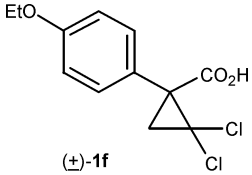
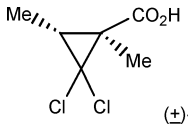
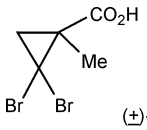
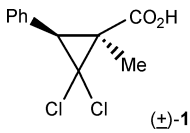
**Fig. 1** X-ray structure of (*S*)-1-phenylethylamide of (1*S*,3*S*)-**1b** (50% probability thermal ellipsoids).

### (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. $Co(dppe)_2Cl_2$ reduction[12] of the corresponding chiral 1,1′-binaphthol esters **3**. Table 3 lists these

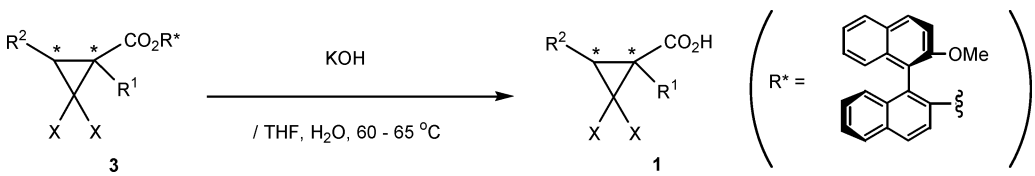
**Table 1** Optical resolution of *gem*-dihalocyclopropanecarboxylic acids (±)-**1** utilizing chiral auxiliary (*R*)-**2**




| Entry | $RCO_2H$ (±)-**1** | Product **3** | $R_f$[a] | Yield (%)[b] | Entry | $RCO_2H$ (±)-**1** | Product **3** | $R_f$ | Yield (%)[b] |
|---|---|---|---|---|---|---|---|---|---|
| 1 |  (±)-**1a** | (1*R*)-**3a**<br>(1*S*)-**3a** | 0.37<br>0.46 | 39<br>41 | 5 |  (±)-**1e** | (1*R*,3*S*)-**3e**<br>(1*S*,3*R*)-**3e** | 0.54<br>0.59 | 37<br>38 |
| 2 |  (±)-**1b** | (1*R*,3*R*)-**3b**<br>(1*S*,3*S*)-**3b** | 0.33<br>0.40 | 39<br>38 | 6 |  (±)-**1f** | (1*R*)-**3f**<br>(1*S*)-**3f** | 0.27<br>0.33 | 39<br>40 |
| 3 |  (±)-**1c** | (1*R*,3*S*)-**3c**<br>(1*S*,3*R*)-**3c** | 0.40<br>0.49 | 39<br>39 | 7 |  (±)-**1g** | (1*R*)-**3g**<br>(1*S*)-**3g** | 0.18[c]<br>0.27[c] | 38<br>39 |
| 4 |  (±)-**1d** | (1*R*,3*S*)-**3d**<br>(1*S*,3*R*)-**3d** | 0.40<br>0.49 | 37<br>36 | | | | | |

[a] Hexane–AcOEt = 5 : 1. [b] Isolated. [c] Hexane–AcOEt = 10 : 1

**Table 2** Hydrolysis of chiral *gem*-dihalocyclopropanecarboxylic esters **3**



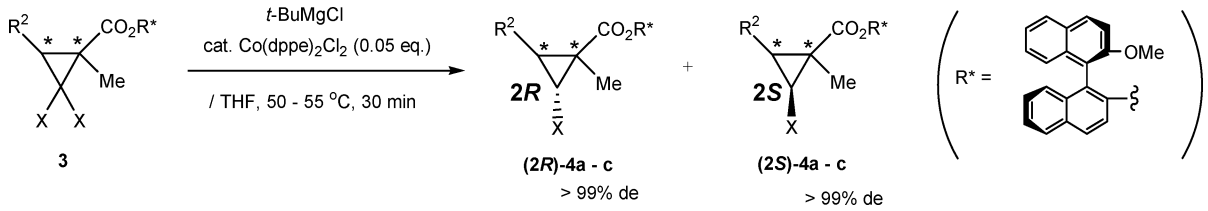

| Entry | $RCO_2R^*$ **3** | Product **1** | Time/h | Yield (%)[a] | Entry | $RCO_2R^*$ **3** | Product **1** | Time/h | Yield (%)[a] |
|---|---|---|---|---|---|---|---|---|---|
| 1 | (1*R*)-**3a** | (1*R*)-**1a** | 4.5 | 93 | 8 | (1*S*,3*R*)-**3d** | (1*S*,3*R*)-**1d** | 3.0 | 82 |
| 2 | (1*S*)-**3a** | (1*S*)-**1a** | 4.5 | 96 | 9 | (1*R*,3*S*)-**3e** | (1*R*,3*S*)-**1e** | 2.5 | 94 |
| 3 | (1*R*,3*R*)-**3b** | (1*R*,3*R*)-**1b** | 15.0 | 92 | 10 | (1*S*,3*R*)-**3e** | (1*S*,3*R*)-**1e** | 2.5 | 95 |
| 4 | (1*S*,3*S*)-**3b** | (1*S*,3*S*)-**1b** | 15.0 | 92 | 11 | (1*R*)-**3f** | (1*R*)-**1f** | 7.0 | 98 |
| 5 | (1*R*,3*S*)-**3c** | (1*R*,3*S*)-**1c** | 5.0 | 89 | 12 | (1*S*)-**3f** | (1*S*)-**1f** | 7.0 | 94 |
| 6 | (1*S*,3*R*)-**3c** | (1*S*,3*R*)-**1c** | 5.0 | 88 | 13 | (1*R*)-**3g** | (1*R*)-**1g** | 6.5 | 89 |
| 7 | (1*R*,3*S*)-**3d** | (1*R*,3*S*)-**1d** | 4.5 | 87 | 14 | (1*S*)-**3g** | (1*S*)-**1g** | 7.0 | 93 |

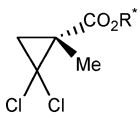
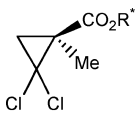
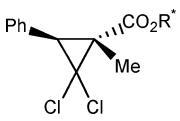
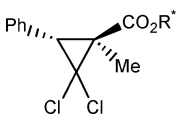
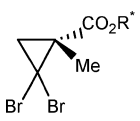
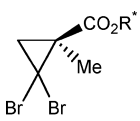
[a] Isolated.

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**.

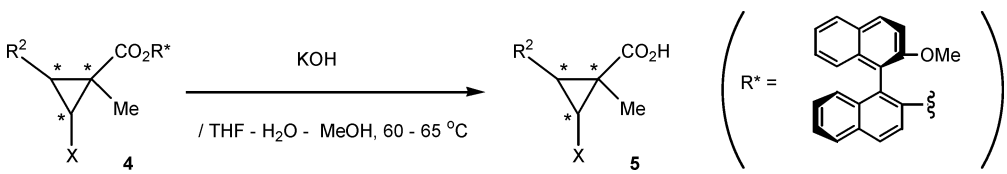
**Table 3** Optical resolution of monohalocyclopropanecarboxylic esters **4a–c** utilizing chiral auxiliary **2**




| Entry | Substrate | *t*-BuMgCl/eq. | Product | 1,2-Configuration | $R_f$[a] | Yield (%)[b] |
|---|---|---|---|---|---|---|
| 1 |  (1*R*)-**3a** | 3.3 | (1*R*,2*R*)-**4a**<br>(1*R*,2*S*)-**4a** | 1,2-*cis*<br>1,2-*trans* | 0.52<br>0.65 | 19<br>51 |
| 2 |  (1*S*)-**3a** | 3.3 | (1*S*,2*R*)-**4a**<br>(1*S*,2*S*)-**4a** | 1,2-*trans*<br>1,2-*cis* | 0.60<br>0.46 | 46<br>24 |
| 3 |  (1*R*,3*S*)-**3b** | 4.0 | (1*R*,2*R*,3S)-**4b**<br>(1*R*,2*S*,3*S*)-**4b** | 1,2-*cis*<br>1,2-*trans* | 0.62<br>0.66 | 40<br>38 |
| 4 |  (1*S*,3*R*)-**3b** | 4.0 | (1*S*,2*R*,3*R*)-**4b**<br>(1*S*,2*S*,3*R*)-**4b** | 1,2-*trans*<br>1,2-*cis* | 0.62<br>0.56 | 40<br>37 |
| 5 |  (1*R*)-**3c** | 1.9 | (1*R*,2*R*)-**4c**<br>(1*R*,2*S*)-**4c** | 1,2-*cis*<br>1,2-*trans* | 0.56<br>0.69 | 35<br>42 |
| 6 |  (1*S*)-**3c** | 1.9 | (1*S*,2*R*)-**4c**<br>(1*S*,2*S*)-**4c** | 1,2-*trans*<br>1,2-*cis* | 0.45<br>0.33 | 40<br>33 |

[a] Hexane–AcOEt = 5 : 1. [b] Isolated.

**Table 4** Hydrolysis of chiral monohalocyclopropanecarboxylic esters **5**

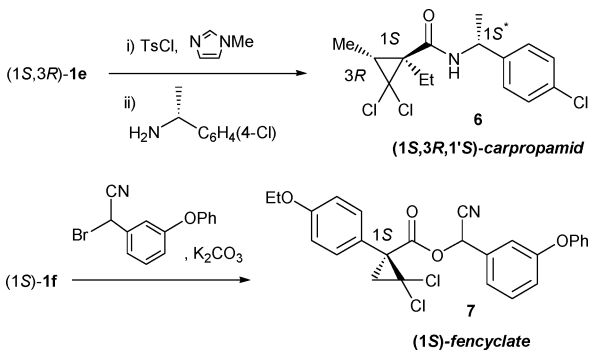



| Entry | $RCO_2R^*$ **4** | Product **5** | Yield (%)[a] | Entry | $RCO_2R^*$ **4** | Product **5** | Yield (%)[a] |
|---|---|---|---|---|---|---|---|
| 1 | (1*R*,2*R*)-**4a** | (1*R*,2*R*)-**5a** | 92 | 7 | (1*S*,2*R*,3*R*)-**4b** | (1*S*,2*R*,3*R*)-**5b** | 93 |
| 2 | (1*R*,2*S*)-**4a** | (1*R*,2*S*)-**5a** | 95 | 8 | (1*S*,2*S*,3*R*)-**4b** | (1*S*,2*S*,3*R*)-**5b** | 92 |
| 3 | (1*S*,2*R*)-**4a** | (1*S*,2*R*)-**5a** | 92 | 9 | (1*R*,2*R*)-**4c** | (1*R*,2*R*)-**5c** | 97 |
| 4 | (1*S*,2*S*)-**4a** | (1*S*,2*S*)-**5a** | 92 | 10 | (1*R*,2*S*)-**4c** | (1*R*,2*S*)-**5c** | 94 |
| 5 | (1*R*,2*R*,3*S*)-**4b** | (1*R*,2*R*,3*S*)-**5b** | 93 | 11 | (1*S*,2*R*)-**4c** | (1*S*,2*R*)-**5c** | 92 |
| 6 | (1*R*,2*S*,3*S*)-**4b** | (1*R*,2*S*,3*R*)-**5b** | 92 | 12 | (1*S*,2*S*)-**4c** | (1*S*,2*S*)-**5c** | 96 |

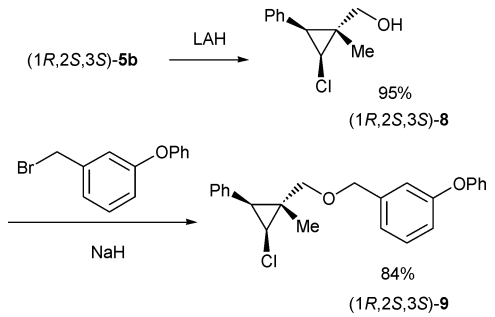
[a] Isolated.

**(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 (1*S*,3*R*)-**1e** with (*S*)-1-(4-chlorophenyl)-ethylamine gave (1*S*,3*R*,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[6b] using thin layer column chromatographic separation of diastereomers derived from (±)-**4a** and (*S*)-1-(4-chlorophenyl)ethylamine. Second, (1*S*)-fencyclate **7**, a synthetic pyrethroid with a unique *gem*-dichlorocyclopropane structure, was readily synthesized by the condensing acid (1*S*)-**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 (1*R*,2*S*,3*S*)-**9**.

A monochlorocyclopropane pyrethroid with three asymmetric centers, (1*R*,2*S*,3*S*)-**9**, was efficiently synthesized (Scheme 5). LAH reduction of (1*R*,2*S*,3*S*)-**5b** gave alcohol (1*R*,2*S*,3*S*)-**8** (95%), which was coupled with 3-phenoxybenzyl bromide to give the desired product (1*R*,2*S*,3*S*)-**9** (84%). Our first synthesis of (1*R*,2*S*,3*S*)-**9** required a tedious optical resolution step for the corresponding racemic acid (1*R**,2*S**,3*S**)-**5b**; four recrystallizations using (*S*)-naphthylethylamine resulted in a poor yield (3.5%) of **5b**.[6b] 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 monohalocyclopropanecarboxylic 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 $^1$H NMR and 75 MHz for $^{13}$C NMR. Chemical shifts ($\delta$ ppm) in $CDCl_3$ were reported downfield from TMS (= 0 ppm) for $^1$H NMR. For $^{13}$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: (1*R*,3*R*)-**3b**, (1*S*,3*S*)-**3b**, (1*R*,3*S*)-**3c**, (1*S*,3*R*)-**3c**, (1*R*,3*S*)-**3d**, (1*S*,3*R*)-**3d**, (1*R*,3*S*)-**3e**, (1*S*,3*R*)-**3e**, (1*R*)-**3f**, (1*S*)-**3f**, (1*R*)-**3g**, (1*S*)-**3g**, (1*S*)-**1a**,[3] (1*R*,3*R*)-**1b**,[5b,c] (1*S*,3*S*)-**1b**,[5b,c] (1*R*,3*S*)-**1c**,[5b,c] (1*S*,3*R*)-**1c**,[5b,c] (1*R*,3*S*)-**1d**,[6b] (1*S*,3*R*)-**1d**,[6b] (1*R*,3*S*)-**1e**, (1*S*,3*R*)-**1e**, (1*R*)-**1f**,[11] (1*S*)-**1f**,[11] (1*R*)-**1g**,[2] (1*S*)-**1g**,[2] (1*S*,2*R*)-**4a**, (1*S*,2*S*)-**4a**, (1*R*,2*R*,3*S*)-**4b**, (1*R*,2*S*,3*S*)-**4b**, (1*S*,2*R*,3*R*)-**4b**, (1*S*,2*S*,3*R*)-**4b**, (1*R*,2*R*)-**4c**, (1*R*,2*S*)-**4c**, (1*S*,2*R*)-**4c**, (1*S*,2*S*)-**4c**, (1*R*,2*S*)-**5a** (1*S*,2*R*)-**5a**, (1*S*,2*S*)-**5a**, (1*R*,2*R*,3*S*)-**5b**, (1*R*,2*S*,3*S*)-**5b**,[6b] (1*S*,2*R*,3*R*)-**5b**,[6b] (1*S*,2*S*,3*R*)-**5b**, (1*R*,2*R*)-**5c**, (1*R*,2*S*)-**5c**, (1*S*,2*R*)-**5c**, and (1*S*,2*S*)-**5c**, are described in the electronic supporting information.†

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

TsCl (127 mg, 0.66 mmol) in $CH_3CN$ (0.60 ml) was added to a stirred solution of (±)-2,2-dichloro-1-methylcyclopropanecarboxylic acid [(±)-**1a**; 112 mg, 0.66 mmol] and *N*-methylimidazole (136 mg, 1.66 mmol) in $CH_3CN$ (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 $CH_3CN$ (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 ($Na_2SO_4$), 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%; $R_f$ = 0.37 (hexane–AcOEt = 5 : 1)] and (1*S*)-**3a** [105 mg, 41%; $R_f$ = 0.46 (hexane–AcOEt = 5 : 1)].

**(1*R*)-3a.** Colorless crystals; $R_f$ = 0.37 (hexane–AcOEt = 5 : 1); mp 141–143 °C; $[\alpha]_D^{24}$ +99.0 (*c* 0.59, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 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). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 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$^{-1}$. HRMS (ESI) calcd for $C_{26}H_{20}Cl_2O_3$ (M + $Na^+$) 473.0687, found 473.0692.

**(1*S*)-3a.** Colorless crystals; $R_f = 0.46$ (hexane–AcOEt = 5 : 1); mp 74–76 °C; $[\alpha]_D^{24}$ −53.1 (*c* 0.66, $CHCl_3$). $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ 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). $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ 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 $cm^{-1}$. HRMS (ESI) calcd for $C_{26}H_{20}Cl_2O_3$ (M + $Na^+$) 473.0687, found 473.0681.

### A typical hydrolysis procedure to give (1*R*)-2,2-dichloro-1-methylcyclopropanecarboxylic acid [(1*R*)-1a][3] (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 $H_2O$ (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 ($Na_2SO_4$) 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 ($Na_2SO_4$) and concentrated to give the desired product (1*R*)-**1a** (1.33 g, 93%).

Yellow oil : $[\alpha]_D^{25}$ +51.4 (*c* 1.77, $CHCl_3$). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 1.48 (1H, d, *Jgem* = 7.6 Hz), 1.16 (3H, s), 2.30 (1H, d, *Jgem* = 7.6 Hz). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 18.02, 31.18, 35.12, 62.61, 175.52. IR (neat) 3001, 1709, 1416, 1316, 945 $cm^{-1}$.

### Preparation[13] 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 $K_2CO_3$ (134 mg, 0.97 mmol) in $CH_3CN$ (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 ($Na_2SO_4$), 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; $[\alpha]_D^{23}$ −35.4 (*c* 0.42, $CHCl_3$). $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ 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). $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 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 $cm^{-1}$.

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

A colorless prismatic single crystal (0.68 × 0.38 × 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$K_\alpha$ 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, β = 101.08 (16)°, *V* = 1522.0 (66) Å$^3$ and $D_{calc.} = 1.249$g $cm^{-3}$. All calculations were performed using the teXsan package.[14] 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 $_wR2$ 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 $CoCl_2(dppe)_2$ (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 ($Na_2SO_4$), 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; $[\alpha]_D^{23}$ +36.9 (*c* 0.35, $CHCl_3$). $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ 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). $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ 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 $cm^{-1}$. HRMS (ESI) calcd for $C_{26}H_{21}ClO_3$ (M + $Na^+$) 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; $[\alpha]_D^{23}$ +46.3 (*c* 3.15, $CHCl_3$). $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ 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). $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ 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 $cm^{-1}$. HRMS (ESI) calcd for $C_{26}H_{21}ClO_3$ (M + $Na^+$) 439.1077, found 439.1078.

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

A mixture of (1*R*,2*R*)-**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 ($Na_2SO_4$) 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 ($Na_2SO_4$), 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, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 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). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 19.3, 23.1, 26.9, 39.5, 177.1. IR (KBr) 2928, 2731, 2617, 1699, 1466, 1422, 1329, 1238, 1209, 941, 909 cm$^{-1}$. Anal. Calcd for $C_5H_7ClO_2$; C, 44.63; H, 5.24, found: C, 44.3; H, 4.9%.

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

TsCl (243 mg, 1.27 mmol) in $CH_3CN$ (1.0 mL) was added to a stirred solution of (1*S*,3*R*)-**1e** (209 mg, 1.06 mmol) and *N*-methylimidazole (241 mg, 3.18 mmol) in $CH_3CN$ (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 $CH_3CN$ (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 ($Na_2SO_4$), 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.[10c] $[a]_D$ +87.9 (MeOH)] $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 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). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 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$^{-1}$ These spectroscopic data completely matched with the reported data.[10c]

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

$Et_3N$ (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 ($Na_2SO_4$), 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; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 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). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 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][6b]

Compound (1*R*,2*S*,3*S*)-**5** (50 mg, 0.10 mmol) in THF was added to a stirred suspension of $LiAlH_4$ (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 $Et_2O$. The combined organic phase was washed with water, brine, dried ($Na_2SO_4$), 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, $CHCl_3$). [lit.[6b] $[a]_D^{23}$ −82.3 (*c* 1.31, $CHCl_3$)]. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 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). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 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$^{-1}$.

### (1*R*,2*S*,3*S*)-2-Chloro-1-methyl-3-phenylcyclopropylmethyl 3-phenoxybenzyl ether [(1*R*,2*S*,3*S*)-9],[6b] a pyrethroid with three asymmetric centers

A mixture of (1*R*,2*S*,3*S*)-**8** (15 mg, 0.08 mmol) and 3-phenoxybenzyl 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 $Et_2O$. The combined organic phase was washed with water, brine, dried ($Na_2SO_4$), 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, $CHCl_3$). [lit.[6b] $[a]_D^{23}$ −48.3 (*c* 1.55, $CHCl_3$)]. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 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). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 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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