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Design, Synthesis, and Insecticidal Activities of Novel Monohalovinylated Pyrethroids

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ABSTRACT: A series of novel monohalovinylated pyrethroids are designed and synthesized to replace one halo atom with a hydrogen atom on the double bond of dihalopyrethroids. Bioassays indicate that some of the synthesized compounds, such as **3j** and **1j**, exhibit high insecticidal activities against mosquitoes (*Culex pipiens pallens*), oriental armyworms (*Mythimna separata*), alfalfa aphids (*Aphis medicagini*), and carmine spider mites (*Tetranychus cinnabarinus*). Photolytic results of *E-cis*-**1j** suggest that monohalovinylated pyrethroids are photodegraded more easily than compound **12**.

KEYWORDS: Pyrethroids, monohalovinylated pyrethroids, insecticide activities, photolysis

INTRODUCTION

In recent years, problems brought about by the use of agricultural chemicals have attracted considerable attention.[1] Increases in population have caused increases in food requirements. These increases have been accompanied by climate warming, pests, and diseases, many of which are transmitted by mosquitoes. Infectious diseases, such as malaria and dengue fever, are on the rise, posing grave threats to human health.[2] Pesticide use has resulted in serious resistance problems, such that increasing dosages are now necessary to eliminate the same number of pests.

In response to these problems, the European Union (EU) implemented a stringent set of standards in 2001 to ensure food safety and testing. For example, the amount of fenvalerate in tea has been limited to 0.05 mg/kg from 0.1 mg/kg, and many pesticides are now limited to below 0.1 mg/kg.[3] It is believed these standards will eliminate the use of most pesticides. In their stead, the new standards encourage the use of highly active, low-residue pesticides. Current pesticide research and agricultural and pesticide production are now faced with the serious challenge of reducing pesticide use in the EU to adapt to new requirements.

Pyrethroids are a kind of biomimetic pesticide with excellent properties, such as high activity, a wide insecticidal spectrum, and low toxicity to humans and other mammals.[4] Research in the field of pyrethroids has generated great excitement in the past several decades.[5] This type of pesticide, however, has two limitations: resistance buildup and high residue formation. As a major product of pyrethroids, cypermethrin has come to be suspected as an endocrine-disrupting compound and is listed in the Our Stolen Future Web site.[6] As well, decamethrin is believed to have mutagenic and teratogenic effects.[7,8]

Careful analysis of the chemical structures of pyrethroids has indicated that dihalopyrethroids, represented by cypermethrin and decamethrin, have high efficiency and low toxicity. It is possible that the poor light stability of the double bonds in these compounds causes the occurrence of overstability phenomena. Thus, with increasing residual time in the environment, teratogenicity, mutagenicity, and endocrine disruption may result. The light stability of monohalopyrethroids is slightly poorer than that of the same structure bearing two halogen atoms, because it deletes one halogen atom having electrophilicity and replaces it with one hydrogen atom having electroneutrality on the double bond. Monohalopyrethroids can be easily photodegraded or biodegraded, thus solving the overstability problem of dihalopyrethroids and generating high efficiency. However, there is a need to improve the low insecticidal activity of this kind of pyrethrate. α-Cyano-3-phenoxybenzyl-2,2-dimethyl-3-(2-halovinyl)cyclopropane carboxylate is detected in only minute quantities in the biodegradation or photodegradation products of cypermethrin and decamethrin and has never been efficiently used.[9,10] Elliott synthesized α-cyano-3-phenoxybenzylmetahalo pyrethrate and pointed out that its insecticidal activity was lower than that of its corresponding α-cyano-3-phenoxybenzyl dihalopyrethrate.[11] Jack also reported some monohalopyrethroids containing fluorine.[12] On the basis of the above analysis and molecular design, we designed and synthesized a series of monohalovinylated pyrethroids (Scheme 1).

MATERIALS AND METHODS

Instruments. Melting points (mp) were recorded on a Yanano MP 500 apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Varian INOVA-500 (500 MHz) spectrometer with $CDCl_3$ as the solvent and TMS as the internal standard. IR spectra were recorded on a Nicolet FT-IR spectrometer. High-resolution mass spectra were recorded under electron impact (70 eV) conditions using a MicroMass GCT CA 055 instrument. GC-MS data were obtained on an Agilent 6890/5973N instrument. Analytical thin-layer chromatography (TLC) was carried out on precoated plates (silica gel 60 F254), and spots were visualized with ultraviolet (UV) light. Ultraviolet irradiation was carried out at 365 nm with two lamps (15 W) in an ultraviolet analyzer (Shanghai Keyi Optical Instrument Factory).

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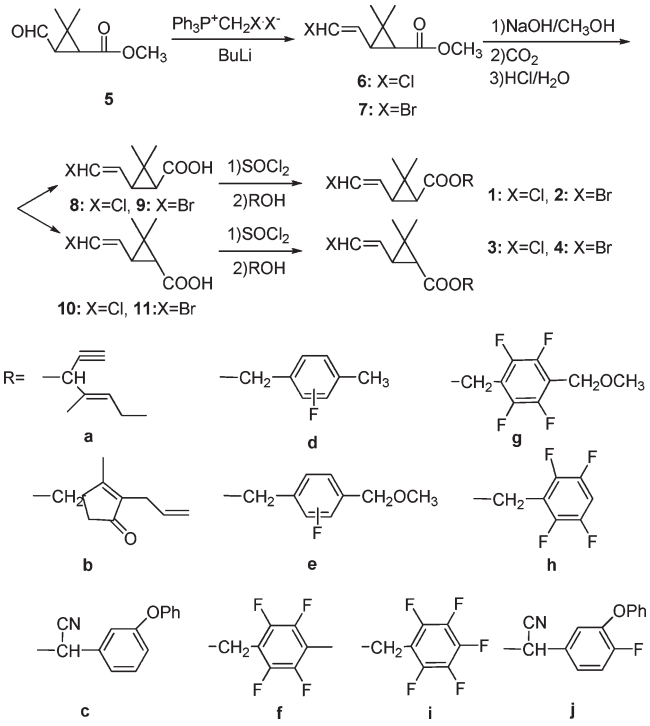
Scheme 1. General Synthetic Procedure for the Target Compounds



Synthetic Procedures. All anhydrous solvents were dried and purified according to standard techniques just before use. Methyl 2,2-dimethyl-3-formylcyclopropanecarboxylate,[13] 2- and 3-fluoro-4-(methoxymethyl)benzyl alcohol,[14] 2- and 3-fluoro-4-methylbenzyl alcohol,[15] 2,3,5,6-tetrafluoro-4-methylbenzyl alcohol, 2,3,5,6-tetrafluoro-4-(methoxymethyl)benzyl alcohol, 2,3,5,6-tetrafluorobenzyl alcohol, and 2,3,4,5,6-pentafluorobenzyl alcohol were synthesized according to literature methods.[16] 4-Hepten-1-yn-3-ol, 2-cyclopenten-1-one, and 3-phenoxybenzaldehyde were provided by Zhongxi Yaoye Corp. Unless otherwise noted, reagents and solvents were used as received from commercial suppliers.

General Synthetic Procedure for 6 and 7. $Ph_3P^+CH_2Cl\ Cl^-$ (2.1 mmol) or $Ph_3P^+CH_2Br\ Br^-$ was added to a round-bottom flask, which was then flushed with nitrogen. Anhydrous ether (20 mL) and piperidine (2.1 mmol) were added to the flask, and the mixture was cooled to −60 to −70 °C by liquid nitrogen. About 9.5 mL of 2.2 mol/L (2.1 mmol) of *n*-BuLi was added to the mixture, which was then allowed to react for 1.5 h. Then, 2.1 mmol of methyl 2, 2-dimethyl-3-formylcyclopropanecarboxylate in 10 mL of benzene was added, and the mixture was stirred for 3 days and 20 min at room temperature. The reaction liquid was washed with 10% of H_2SO_4 solution in brine and dried. The solvent was removed under reduced pressure, and the crude product was purified by column chromatography to give a colorless liquid.

Data for ***6***:. yield, 58%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.18, 1.20 (2s, 3H, cyclo-CH_3), 1.25, 1.28 (2s, 3H, cyclo-CH_3), 1.56−1.58 (m, 1H, cyclo-H), 2.04−2.05 (m, 1H, cyclo-H), 3.68, 3.69 (2s, 3H, $COOCH_3$), 5.47−5.70 (m, 1H, =CH), 6.06−6.14 (m, 1H, =CHCl); IR (KBr, cm^{-1}) 1725, 1409, 1150.

Data for ***7***:. yield, 40%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.19, 1.21 (2s, 3H, cyclo-CH_3), 1.25, 1.29 (2s, 3H, cyclo-CH_3), 1.62−1.65 (m, 1H, cyclo-H), 2.05−2.20 (m, 1H, cyclo-H), 3.69, 3.70 (2s, 3H, $COOCH_3$), 5.85−5.97 (m, 1H, =CH), 6.16−6.30 (m, 1H, =CHBr); IR (KBr, cm^{-1}) 1728, 1407, 1173.

General Synthetic Procedure for 8−11. A mixture of sodium hydroxide (125 mmol), water (15 mL), methanol (50 mL), 86 mmol of methyl 3-(2-halovinyl)-2,2-dimethylcyclopropanecarboxylate (**6** or **7**), and tetrabutylammonium bromide (1 g) was stirred for 5 h at reflux, after which the solvent was removed in vacuo. The residue was dissolved in 30 mL of water, and CO_2 gas was passed into the system continuously at room temperature for 4 h. The mixture was extracted with diethyl ether (50 mL × 3). The combined extracts were washed with saturated brine and dried with anhydrous magnesium, and the solvent was removed in vacuo to obtain a sticky brown product (*cis*-**8** or *cis*-**9**). The residual water layer was acidified with 10% HCl and purified to obtain the *trans*-isomers as yellow liquid (*trans*-**10** or *trans*-**11**).

Data for ***8***:. recrystallized in hexane to give a white solid; mp 84−94 °C; *E-cis*/*Z-cis* = 6:4; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.20 (s, 0.4 × 6H, cyclo-CH_3), 1.27 (s, 0.6×6H, cyclo-CH_3), 1.73 (d, 0.6×1H, J = 8.0 Hz, cyclo-CH), 1.82 (d, 0.4 × 1H, J = 8.0 Hz, cyclo-CH), 1.90 (dd, 0.6 × 1H, J_1 = 8.0 Hz, J_2 =10.0 Hz, cyclo-CH), 2.32 (dd, 0.4 × 1H, J_1 = 8.0 Hz, J_2 = 8.5 Hz, cyclo-CH), 6.08 (d, 0.6×1H, J = 13.0 Hz, (*E*)ClHC=), 6.10 (dd, 0.4 × 1H, J_1 = 8.5 Hz, J_2 =7.5 Hz, (*Z*)HC=), 6.15 (d, 0.4 × 1H, J = 7.5 Hz, (*Z*)ClHC=), 6.22 (dd, 0.6 × 1H, J_1 =10.0 Hz, J_2 = 13.0 Hz, (*E*)CH=), 11.97 (s, 1H, COOH); IR (KBr, cm^{-1}) 2964, 1692, 1225, 937.

Data for ***9***:. yellow liquid; *E-cis*/*Z-cis* = 6:4; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.22 (s, 0.4 × 6H, cyclo-CH_3), 1.29, 1.31 (2s, 0.6×6H, cyclo-CH_3), 1.75 (d, 0.6 × 1H, J = 8.0 Hz, cyclo-CH), 1.85 (d, 0.4 ×1H, J = 9.0 Hz, cyclo-CH), 1.91 (dd, 0.6 × 1H, J_1 = J_2 = 9.0 Hz, cyclo-CH), 2.23−2.28 (dd, 0.4 × 1H, J_1 = 9.0 Hz, J_2 = 7.0 Hz, cyclo-CH), 6.17 (d, 0.6 × 1H, J = 13.0 Hz, (*E*)BrHC=), 6.30 (d, 0.4 × 1H, J = 7.0 Hz, (*Z*)BrHC=), 6.45 (dd, 0.4 × 1H, J_1 = J_2 = 7.0 Hz, (*Z*)CH=), 6.49 (dd, 0.6 × 1H, J_1 = 9.0 Hz, J_2 = 13.0 Hz, (*E*)CH=), 11.59 (s, 1H, −COOH); IR (KBr, cm^{-1}) 1703, 1215, 938.

Data for ***10***:. yellow liquid; *E-trans*/*Z-trans* = 7:3; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.21, 1.28 (2s, 2×3H, cyclo-CH_3), 1.60−1.62 (m, 0.7 × 1H, cyclo-CH), 1.74 (d, 0.3×1H, J = 5.0 Hz, cyclo-CH), 2.07−2.10 (m, 0.7 × 1H, cyclo-CH), 2.44−2.46 (m, 0.3× 1H, cyclo-CH), 5.46 (dd, 0.3 × 1H, J_1 = J_2 = 7.0 Hz, (*Z*)CH=), 5.66−5.08 (dd, 0.7 × 1H, J_1 = J_2 = 13.0 Hz, (*E*)CH=), 6.08−6.11 (d, 0.7×1H, J = 13.0 Hz, (*E*)ClHC=), 6.15−6.16 (d, 0.3×1H, J=7.0 Hz, (*Z*)ClHC=), 11.68 (s, 1H, −COOH); IR (KBr, cm^{-1}) 2966, 1690, 1220, 935.

Data for ***11***:. yellow liquid; *E-trans*-isomer/*Z-trans*-isomer = 6:4; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.21 (s, 0.6×3H, cyclo-CH_3), 1.26 (s, 0.4× 3H, cyclo-CH_3), 1.29 (s, 0.6 × 3H, cyclo-CH_3), 1.36 (s, 0.4×3H, cyclo-CH_3), 1.60−1.63 (d, 0.6 × 1H, J = 4.0 Hz, cyclo-H), 1.98 (d, 0.4×1H, J = 4.0 Hz, cyclo-H), 2.08−2.10 (m, 0.6 × 1H, cyclo-H), 2.38−2.41 (m, 0.4 × 1H, cyclo-H), 5.86−5.89 (dd, 0.4 × 1H, J_1 = J_2 = 7.0 Hz, (*Z*)CH=), 5.92−5.97 (dd, 0.6 × 1H, J_1 = J_2 = 14.0 Hz, (*E*)CH=), 6.19(d, 0.6 × 1H, J = 14.0 Hz, (*E*)BrHC=), 6.31 (d, 0.4 × 1H, J = 7.0 Hz, (*Z*)BrHC=), 10.5(b, 1H, COOH); IR (KBr, cm^{-1}) 1703, 1215, 938.

General Synthetic Procedure for 1a−c, 1f, 1h−j, 2a−c, 3c−j, and 4d, and 4e. A mixture of monohalovinylated acid (5.7 mmol) and thionyl chloride (5.0 mL) was heated to 50 °C for 4−5 h. The excess thionyl chloride was removed in vacuo, and the residue was diluted with benzene (5.0 mL) for use. To a solution of alcohol (5.7 mmol) and pyridine (0.8 mL) in benzene (10 mL) was slowly added the acyl chloride solution prepared abovein an ice−water bath for 30 min. The mixture was stirred overnight, and then 10 mL of water was added. The organic phase was separated and washed successively with 10 mL of 5% NaOH solution, 5% of hydrochloric acid solution and brine, and dried with Na_2SO_4. The solvent was removed to give a yellow and viscous product. The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 20:1) to afford a light yellow liquid.

Data for ***1a***:. yield, 72%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.98 (t, 3H, J_1 =J_2 = 8.0 Hz, CH_3), 1.18 (s, 3H, cyclo-CH_3), 1.26, 1.29 (2s, 3H, cyclo-CH_3), 1.73 (s, 3H, =CH_3), 1.77 (d, 1H, J = 9.0 Hz, cyclo-CH),

1.81−1.86 (m, 1H, cyclo-CH), 2.05−2.08 (m, 2H, $-CH_2-$), 2.52 (s, 1H, CH≡), 5.69 (dd, 1H, $J_1 = J_2 = 7.0$ Hz, =CH—Et), 5.74, 5.76 (2s, 1H, COOCH), 6.05 (dd, 1H, $J_1 = 4.5$ Hz, $J_2 = 13.5$ Hz, ClHC=), 6.22−6.29 (m, 1H, CH=); IR (KBr, cm^{-1}) 3298, 2963, 2932, 2875, 1729, 1409, 1365, 1175, 1132, 1079; HRMS calcd for $C_{16}H_{21}O_2{}^{35}Cl$ (M^+), 280.1231; found, 280.1236.

Data for **1b**:. yield, 76%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.14, 1.20, 1.21, 1.22 (4s, 6H, cyclo-CH_3), 1.69 (d, 0.6H, $J = 8.0$ Hz, cyclo-CH), 1.79−1.82 (m, 1H, cyclo-CH), 1.94 (2s, 3H, =CH_3), 2.17−2.23 (m, 1.4H, cyclo-CH, $COCH_2$), 2.73−2.81 (m, 1H, $COCH_2$), 2.91 (d, 2H, $J = 6.0$ Hz, =CH_2), 4.93−4.96 (m, 2H, =CH_2), 5.59−5.73 (m, 2H, COOCH, CH_2=CH), 5.99−6.21 (m, 2H, HCl=CH); IR (KBr, cm^{-1}) 1715, 1655, 1413, 1170, 1132, 1081; HRMS calcd for $C_{17}H_{23}O_3{}^{35}Cl$ (M^+), 310.1337; found, 310.1335.

Data for **1c**:. yield, 85%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.20,1.22 (2s, 0.4 × 6H, cyclo-CH_3), 1.25,1.32 (2s, 0.6×6H, cyclo-CH_3), 1.81 (dd, 1H, $J_1 = J_2 = 8.0$ Hz, cyclo-CH), 1.91−1.98 (m, 1H, cyclo-CH), 6.11 (dd, 1H, $J_1 = 7.0$ Hz, $J_2 = 13.0$ Hz, ClHC=), 6.18−6.23 (m, 1H, =CH), 6.34 (s, 0.6×1H, CH—CN), 6.40 (s, 0.4 × 1H, CH—CN), 7.03−7.07 (m, 3H, ArH), 7.15−7.18 (m, 2H, ArH), 7.23−7.26 (m, 1H, ArH), 7.37−7.42 (m, 3H, ArH); IR (KBr, cm^{-1}) 3446, 3071, 2959, 1741, 1588, 1487, 1244, 1122, 1073; HRMS calcd for $C_{22}H_{20}NO_3{}^{35}Cl$ (M^+), 381.1133; found, 381.1131.

Data for **1i**:. yield, 85%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.19−1.28 (4s, 6H, cyclo-CH_3), 1.69,1.71 (2d, 1H, $J_1 = J_2 = 8.0$ Hz, cyclo-CH), 1.84 (m, 1H, cyclo-CH), 5.15−5.25 (m, 2H, $COOCH_2$), 5.92 (d, 0.4 × 1H, $J = 8.0$ Hz, (*Z*)ClHC=), 6.06 (d, 0.6 × 1H, $J = 14.0$ Hz, (*E*)ClHC=), 6.23 (m, 1H, HC=); IR (KBr, cm^{-1}) 3031, 2961, 1725, 1611; HRMS calcd for $C_{15}H_{12}O_2{}^{35}ClF_5$ (M^+), 354.0446; found, 354.0449.

Data for **1h**:. yield, 63%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.21−1.29 (4s, 6H, cyclo-CH_3), 1.77 (dd, 1H, $J_1 = J_2 = 9.0$ Hz, cyclo-CH), 1.84−1.91 (m, 1H, cyclo-CH), 5.09−5.15 (q, 2H, $J = 3.0$ Hz, $COOCH_2$), 5.93 (d, 0.4 × 1H, $J = 8.0$ Hz, (*Z*)ClHC=), 6.06 (d, 0.6 × 1H, $J = 13.0$ Hz, (*E*)ClHC=), 6.21−6.25 (m, 1H, HC=), 7.02−7.07 (m, 1H, ArH); IR (KBr, cm^{-1}) 3001, 2801, 1730, 1633; HRMS calcd for $C_{15}H_{13}O_2{}^{35}ClF_4$ (M^+), 336.0541; found, 336.0547.

Data for **1f**:. yield, 75%; ^{1}H NMR (500 MHz,$CDCl_3$) δ 1.19−1.28 (4s, 6H, cyclo-CH_3), 1.70 (dd, 1H, $J_1 = J_2 = 9$ Hz, cyclo-CH), 1.83 (m, 1H, cyclo-CH), 2.28−2.29 (m, 3H, $ArCH_3$), 5.15 (q, 2H, $J = 3.0$ Hz, $COOCH_2$), 6.05 (dd, 1H, $J_1 = 13.0$ Hz, $J_2 = 8.0$ Hz, ClHC=), 6.21 (m, 1H, HC=); IR (KBr, cm^{-1}) 2934, 2876, 1720, 1601; HRMS calcd for $C_{16}H_{15}O_2{}^{35}ClF_4$ (M^+), 350.0697; found, 350.0703.

Data for **1j**:. yield, 82%; ^{1}H NMR (500 MHz $CDCl_3$) δ 1.16, 1.18 (2s, 0.4 × 6H, cyclo-CH_3), 1.21, 1.28 (2s, 0.6×6H, cyclo-CH_3), 1.77 (m, 1H, cyclo-CH), 1.89−1.90 (m, 1H, cyclo-CH), 6.06 (m, 1H, ClHC=), 6.14−6.20 (m, 1H, =CH), 6.27−6.32 (2s, 1H, CH—CN), 6.98−6.99 (m, 2H, ArH), 7.11−7.14 (m, 1H, ArH), 7.19−7.27 (m, 3H, ArH), 7.32−7.35 (m, 2H, ArH); IR (KBr, cm^{-1}) 1728, 1587, 1487, 1241, 1122, 998; HRMS calcd for $C_{22}H_{19}NO_3{}^{35}ClF$ (M^+), 399.1037; found, 399.1035.

Data for **2a**:. yield, 73%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.97−1.00 (m, 3H, CH_3), 1.24, 1.27, 1.30 (3s, 6H, cyclo-CH_3), 1.74 (d, 3H, $J = 4.0$ Hz, =CH_3), 1.87 (d, 1H, $J = 9.0$ Hz, cyclo-CH), 2.04−2.11 (m, 2H, $-CH_2-$), 2.20 (m, 1H, cyclo-CH), 2.51−2.52 (m, 1H, ≡CH), 5.70 (m, 1H, =CH_2—Et), 5.74, 5.76 (2s, 1H, COOCH), 6.28 (dd, 1H, $J_1 = 6$ Hz, $J_2 = 12$ Hz, BrHC=), 6.47−6.51 (m, 1H, CH=); IR (KBr, cm^{-1}) 3296, 2965, 2869, 1728, 1407, 1173, 1131. HRMS calcd for $C_{16}H_{21}O_2{}^{79}Br$ (M^+), 324.0725; found, 324.0729.

Data for **2b**:. yield, 77%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.18−1.28 (m, 2 × 3H, cyclo-CH_3), 1.74−1.76 (m, 0.6 × 1H, cyclo-CH), 1.83−1.88 (m, 1H, cyclo-CH), 2.00(s, 3H, =CH_3), 2.18−2.27 (m, 1.4 × 1H, cyclo-CH, $COCH_2$), 2.79−2.87 (m, 1H, $COCH_2$), 2.97 (d, 2H, $J = 7.0$ Hz, =CH_2), 4.99 (d, 1H, $J = 10.0$ Hz, =CH_2), 5.00 (d, 1H, $J = 18.0$ Hz, =CH_2), 5.64−5.79 (m, 2H, COOCH, —CH=), 6.15 (dd, 0.6 × 1H, $J_1 = J_2 = 13.0$ Hz, (*E*)CH=), 6.28−6.30 (m, 0.4 × 1H, (*Z*)CH=), 6.40−6.52 (m, 1H, BrHC=); IR (KBr, cm^{-1}) 1714, 1656, 1384, 1156; HRMS calcd for $C_{17}H_{23}O_3{}^{79}Br$ (M^+), 354.0831; found, 354.0835.

Data for **2c**:. yield, 85%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.12−1.25 (m, 6H, cyclo-CH_3), 1.74 (d, 0.6 × 1H, $J = 8.0$ Hz, cyclo-CH), 1.82−1.91 (m, 1H, cyclo-CH), 2.24 (m, 0.4 × 1H, cyclo-CH), 6.09 (d, 0.4 × 1H, $J = 13.0$ Hz, (*Z*)BrCH=), 6.14 (d, 0.6 × 1H, $J = 8.0$ Hz, (*E*)BrCH=), 6.26, 6.32 (2s, 1H, CH—CN), 6.36−6.99 (m, 1H, CH=), 6.95−6.99 (m, 3H, ArH), 7.07−7.10 (m, 2H, ArH), 7.15−7.18 (m, 1H, ArH), 7.28−7.34 (m, 3H, ArH); IR (KBr, cm^{-1}) 3064, 2961, 1745, 1586, 1478, 1448, 1246, 1109, 693; HRMS calcd for $C_{22}H_{20}NO_3{}^{79}Br$ (M^+), 425.0627; found, 425.0621.

Data for **3c**:. yield, 85%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.19, 1.20, 1.27, 1.30 (4s, 6H, cyclo-CH_3), 1.66−1.68 (m, 1H, cyclo-CH), 2.12−2.17 (m, 1H, cyclo-CH), 5.51−5.72 (m, 1H, CH=), 6.09−6.22 (m, 1H, ClHC=), 6.38, 6.43 (2s, 1H, CH—CN), 7.03−7.07 (m, 3H, ArH), 7.13−7.18 (m, 2H, ArH), 7.24−7.26 (m, 1H, ArH), 7.36−7.42 (m, 3H, ArH); IR (KBr, cm^{-1}) 3439, 2948, 1725, 1570, 1207, 1069; HRMS calcd for $C_{22}H_{20}NO_3{}^{35}Cl$ (M^+), 381.1133; found, 381.1136.

Data for **3d**:. yield, 57%; ^{1}H NMR (500 MHz,$CDCl_3$) δ 1.16, 1.18, 1.24, 1.26 (4s, 6H, cyclo-CH_3), 1.60−1.63 (m, 0.7 × 1H, cyclo-H), 1.78−1.90 (m, 0.7 × 1H, cyclo-CH), 1.96 (m, 0.3 × 1H, cyclo-CH), 2.07 (m, 0.3 × 1H, cyclo-CH), 2.27 (s, 0.7 × 3H, Ar—CH_3), 2.35 (s, 0.3 × 3H, Ar—CH_3), 5.05−5.08 (m, 0.7 × 2H, $COOCH_2$), 5.13−5.17 (m, 0.3 × 2H, $COOCH_2$), 5.50 (dd, 0.3 × 1H, $J_1 = 8$ Hz, $J_2 = 7.0$ Hz, (*Z*)CH=), 5.64−5.69 (m, 0.7 × 1H, (*E*)CH=), 6.08 (dd, 0.7 × 1H, $J_1 = J_2 = 13.0$ Hz, (*E*)ClHC=), 6.14 (d, 0.3 × 1H, $J = 7.0$ Hz, (*Z*)ClHC=), 6.89−6.95 (m, 1H, ArH), 6.98−7.04 (m, 1H, ArH), 7.15−7.26 (m, 1H, ArH); IR (KBr, cm^{-1}) 1726, 1631, 1473, 1401, 1384, 1115,982; HRMS calcd for $C_{16}H_{18}O_2{}^{35}ClF$ (M^+), 296.0980; found, 296.0988.

Data for **3e**:. yield, 53%; ^{1}H NMR (500 MHz,$CDCl_3$) δ 1.23 (s, 3H, cyclo-CH_3), 1.30, 1.33 (2s, 3H, cyclo-CH_3), 1.81−1.85 (m, 1H, cyclo-CH), 1.90−1.96 (m, 1H, cyclo-CH), 3.45, 3.46 (2s, 3H, OCH_3), 4.50, 4.57 (2s, 2H, $ArCH_2$), 5.12−5.21 (m, 2H, $COOCH_2$), 5.67−5.73 (m, 0.3 × 1H, (*Z*)CH=), 6.12 (d, 0.7 × 1H, $J = 13.0$ Hz, (*E*)ClCH=), 6.19 (d, 0.3 × 1H, $J = 7.0$ Hz, (*Z*)ClHC=), 6.32 (dd, 0.7 × 1H, $J_1 = J_2 = 13.0$ Hz, (*E*)HC=), 7.10−7.18 (m, 2H, ArH), 7.39−7.46 (m, 1H, ArH); IR (KBr, cm^{-1}) 1726, 1631, 1401, 1384, 1100, 1003, 980; HRMS calcd for $C_{17}H_{20}O_3{}^{35}ClF$ (M^+), 326.1086; found, 326.1082.

Data for **3f**:. yield, 75%; ^{1}H NMR (500 MHz,$CDCl_3$) δ 1.16 (s, 3H, cyclo-CH_3), 1.24 (s, 3H, cyclo-CH_3), 1.55 (d, 1H, $J = 6.0$ Hz, cyclo-CH), 2.05−2.08 (m, 0.7 × 1H, cyclo-CH), 2.29 (s, 3H, $ArCH_3$), 2.41−2.43 (m, 0.3 × 1H, cyclo-CH), 5.16−5.19 (m, 2H, $COOCH_2$), 5.47 (t, 0.3 × 1H, $J = 8.0$ Hz, (Z)CH=), 5.66 (dd, 0.7 × 1H, $J_1 = J_2 = 13.0$ Hz, (*E*)CH=), 6.06 (d, 0.7 × 1H, $J = 13.0$ Hz, (*E*)ClHC=), 6.14 (d, 0.3 × 1H, $J = 8.0$ Hz, (*Z*)ClHC=); IR (KBr, cm^{-1}) 3010, 2716, 1740, 1636, 1384; HRMS calcd for $C_{16}H_{15}O_2{}^{35}ClF_4$ (M^+), 350.0697; found, 350.0701.

Data for **3g**:. yield, 84%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.17 (s, 3H, cyclo-CH_3), 1.25 (s, 3H, cyclo-CH_3), 1.58 (d, 1H, $J = 5.5$ Hz, cyclo-CH), 2.07 (dd, 0.7 × 1H, $J_1 = 5.5$ Hz, $J_2 = 9.0$ Hz, cyclo-CH), 2.41 (dd, 0.3 × 1H, $J_1 = 5.5$ Hz, $J_2 = 8.5$ Hz, cyclo-CH), 3.40 (s, 0.7 × 3H, OCH_3), 3.42 (s, 0.3 × 3H, OCH_3), 4.52 (s, 0.3 × 2H, $ArCH_2$), 4.58 (s, 0.7 × 2H, $ArCH_2$), 5.19−5.26 (m, 2H, $COOCH_2$), 5.45 (t, 0.3×1H, $J = 8.0$ Hz, (*Z*)CH=), 5.65 (dd, 0.7 × 1H, $J_1 = 13.0$ Hz, $J_2 = 9.0$ Hz, (*E*)CH=), 6.08 (d, 0.7 × 1H, $J = 13.0$ Hz, (*E*)ClHC=), 6.16 (d, 0.3×1H, $J = 8.0$ Hz, (*Z*) ClHC=); IR (KBr, cm^{-1}) 2933, 2862, 1722, 1603; HRMS calcd for $C_{17}H_{17}O_3{}^{35}ClF_4$ (M^+), 380.0803; found, 380.0809.

Data for **3h**:. yield, 70%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.17, 1.23 (2s, 3H, cyclo-CH_3), 1.25, 1.32 (2s, 3H, cyclo-CH_3), 1.61 (d, 1H, $J = 5.0$ Hz, cyclo-CH), 2.07−2.09 (m, 0.7×1H, cyclo-CH), 2.41−2.43 (m, 0.3× 1H, cyclo-CH), 5.13−5.15 (m, 2H, $COOCH_2$), 5.49 (t, 0.3 × 1H, $J = 8.0$ Hz, (Z)CH=), 5.65 (dd, 0.7 × 1H, $J_1 = J_2 = 14.0$ Hz, (*E*)CH=), 6.08 (d, 0.7 × 1H, J = 14.0 Hz, (*E*) ClHC=), 6.16 (d, 0.3 × 1H, $J = 8.0$ Hz, (*Z*) ClHC=), 7.02−7.07 (m, 1H, ArH); IR (KBr, cm^{-1}) 2929, 2828, 17

Table 1. Insecticidal Activities of the Title Compounds, Deltamethrin, and Cypermethrin against Mosquitoes (*Culex pipiens pallens*)[a]

compd	LC_{50}(mg/L) (95% fiducial limit)	LC_{95}(mg/L) (95% fiducial limit)	toxic ratio[b]	compd	LC_{50}(mg/L) (95% fiducial limit)	LC_{95}(mg/L) (95% fiducial limit)	toxic ratio
1a	0.3290 (0.2926−0.3698)	1.0957 (0.9599−1.2779)	3.2	**3d**	0.6049 (0.5791−0.6319)	0.9465 (0.8945−1.0223)	1.8
1b	0.3899 (0.3675−0.4137)	0.7164 (0.6209−0.8782)	2.7	**3e**	0.7495 (0.7103−0.7909)	1.3021 (1.1452−1.8139)	1.4
1c	0.0048 (0.0043−0.0052)	0.0127 (0.0114−0.0147)	220.8	**3f**	0.0578 (0.0553−0.0603)	0.0900 (0.0804−0.1186)	18
1f	0.0741 (0.0699−0.0786)	0.1354 (0.1200−0.2128)	14.3	**3g**	0.2025 (0.1876−0.2187)	0.4461 (.3471−3.7111)	5.2
1i	0.0801 (0.0756−0.0850)	0.1476 (0.1360−0.1555)	13.2	**3h**	0.2492 (0.2394−0.2594)	0.3580 (0.3378−0.6238)	4.3
1h	0.4810 (0.4621−0.5006)	0.7262 (0.6197−1.1865)	2.2	**3i**	0.2041 (0.1991−0.2093)	0.2639 (0.2553−0.2762)	5.2
1j	0.00047 (0.00042−0.00054)	0.00168 (0.00076−0.00326)	2255.3	**3j**	0.0055 (0.0042−0.0072)	0.0861 (0.0746−0.0991)	192.7
2a	0.2809 (0.2711−0.2909)	0.4033 (0.3866−0.4296)	3.8	**4d**	0.2133 (0.1987−0.2289)	0.4405 (0.3641−0.7863)	5.0
2b	0.4403 (0.4206−0.4610)	0.7054 (0.6272−0.9126)	2.4	**4e**	0.2776 (0.2589−0.2976)	0.5681 (0.4563−0.9448)	3.8
2c	0.0108 (0.0101−0.0116)	0.0221 (0.0198−0.0393)	98	deltamethrin	0.0012 (0.0008−0.0018)	0.0033 (0.0031−0.0035)	883
3c	0.0527 (0.0484−0.0574)	0.1268 (0.0874−0.5697)	20	cyperethrin	0.0106 (0.0094−0.0119)	0.0286 (0.0232−0.0354)	100

[a] The insecticidal activity report was provided by Shanghai Manyi Science and Technology Co. Ltd. [b] Toxic ratio is defined as the ratio of cypermethrin's LC_{50} value for baseline toxicity and the compounds' LC_{50} values.

27, 1619; HRMS calcd for $C_{15}H_{13}O_2{}^{35}ClF_4$ (M^+), 336.0541; found, 336.0544.

Data for ***3i***:. yield, 71%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.17, 1.24 (2s, 3H, cyclo-CH_3), 1.25, 1.31 (2s, 3H, cyclo-CH_3), 1.58 (d, 0.7 × 1H, J = 5.0 Hz, cyclo-CH), 2.06−2.09 (m, 0.7 × 1H, cyclo-CH), 2.41−2.43 (m, 0.3 × 1H, cyclo-CH), 5.17−5.19 (m, 2H, $COOCH_2$), 5.48 (t, 0.3 × 1H, J = 7 Hz, (*Z*)CH═), 5.64 (dd, 0.7 × 1H, $J_1 = J_2$ = 13.0 Hz, (*E*)CH═), 6.07 (d, 0.7 × 1H, J = 13.0 Hz, (*E*)ClHC═), 6.15 (d, 0.3 × 1H, J = 8.0 Hz, (*Z*)ClHC═); IR (KBr, cm^{-1}) 3128, 2962, 1736, 1656, 970; HRMS calcd for $C_{15}H_{12}O_2{}^{35}ClF_5$ (M^+), 354.0446; found, 354.0442.

Data for ***3j***:. yield, 80%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.18−1.29 (m, 6H, cyclo-CH_3), 1.61−1.64 (m, 1H, cyclo-CH), 2.12−2.15 (m, 1H, cyclo-CH), 5.64−5.70 (m, 1H, CH═), 6.12 (m, 1H, HClC═), 6.31 (s, 0.3 × 1H, CH—CN), 6.33 (s, 0.7 × 1H, CH—CN), 7.01−7.02 (m, 2H, ArH), 7.15−7.20 (m, 2H, ArH), 7.25−7.30 (m, 2H, ArH), 7.36−7.39 (m, 2H, ArH); IR (KBr, cm^{-1}) 1721, 1588, 1500, 1244, 1102, 1073; HRMS calcd for $C_{22}H_{19}NO_3{}^{35}ClF$ (M^+), 399.1037; found, 399.1039.

Data for ***4d***:. yield, 85%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.17, 1.18 (2s, 3H, cyclo-CH_3), 1.24, 1.30 (2s, 3H, cyclo-CH_3), 1.63−1.66 (m, 1H, cyclo-CH), 2.05−2.08 (m, 0.6 × 1H, cyclo-CH), 2.26 (s, 0.4 × 3H, Ar—CH_3), 2.34 (s, 0.6 × 3H, Ar—CH_3), 2.36−2.40 (m, 0.4 × 1H, cyclo-H), 5.02−5.08 (m, 0.6 × 2H, $COOCH_2$), 5.10−5.16 (m, 0.4 × 2H, $COOCH_2$), 5.85 (d, 0.4 × 1H, J = 8.0 Hz, (*Z*)CH═), 5.90−5.95 (m, 0.6 × 1H, (*E*)CH═), 6.15 (d, 0.6 × 1H, J = 14.0 Hz, (*E*)BrHC═), 6.28 (d, 0.4 × 1H, J = 8.0 Hz, (*Z*)BrHC═), 6.88−6.95 (m, 1H, ArH), 7.00−7.03 (m, 1H, ArH), 7.14−7.28 (m, 1H, ArH); IR (KBr, cm^{-1}) 1726, 1631, 1401, 1384, 1003, 939; HRMS calcd for $C_{16}H_{18}O_2{}^{79}BrF$ (M^+), 340.0474; found, 340.0479.

Data for ***4e***:. yield, 88%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.17, 1.19 (2s, 3H, cyclo-CH_3), 1.25, 1.32 (2s, 3H, cyclo-CH_3), 1.63−1.68 (m, 1H, cyclo-H), 2.07−2.09 (m, 0.6 × 1H, cyclo-H), 2.38−2.41 (m, 0.4 × 1H, cyclo-H), 3.40, 3.41 (2s, 3H, OCH_3), 4.45, 4.52 (s, 2H, $ArCH_2$), 5.08−5.17 (m, 2H, $COOCH_2$), 5.87 (t, 0.4 × 1H, J = 8.0 Hz, (*Z*)CH═), 5.90−5.96 (m, 0.6 × 1H, (*E*)CH═), 6.15−6.19 (dd, 0.6 × 1H, $J_1 = J_2$ = 14.0 Hz, (*E*)BrHC═), 6.29 (d, 0.4 × 1H, J = 7.0 Hz, (*Z*)BrHC═), 7.05−7.15 (m, 2H, ArH), 7.34−7.42 (m, 1H, ArH); IR (KBr, cm^{-1}) 1728, 1636, 1400, 1384, 1158, 1114, 1002; HRMS calcd for $C_{17}H_{20}O_3{}^{79}BrF$ (M^+), 370.0580; found, 370.0585.

Biological Assay. Bioassays were conducted with four insect species, mosquito (*Culex pipiens pallens*) (Shanghai Manyi Science and Technology Co. Ltd.), armyworm (*Mythimna separata*), aphid (*Aphis craccivora*), and carmine spider mites (*Tetranychus cinnabarinus*) (Shanghai Southern Pesticides Research Center, China). All bioassays were performed on representative test organisms reared in the laboratory. The bioassay was repeated at 26 ± 1 °C and 70 ± 10% relative humidity according to statistical requirements. All compounds were dissolved in acetone and diluted with water to obtain series concentrations for bioassays. Each concentration was tested three times in parallel. Concentrations of 500.0, 50.0, and 5.0 mg L^{-1} and others for mosquitoes, 500.0, 50.0, 5.0,1.0, 0.5, and 0.25 mg L^{-1} for armyworms and aphids, and 500.0, 50.0, 5.0, and 1.0 mg L^{-1} for spider mites were used. For comparative purposes, cypermethrin and decamethrin were tested under the same conditions.

Insecticidal Test for Mosquito. The activities of insecticidal compounds against mosquito were tested by the dipping method according to the reported procedure.[17,18] Twenty-five fourth-instar mosquito larvae (wrigglers) were put into appropriate solutions of the tested compounds, and the mortality rates were evaluated 24 h after treatment.

Insecticidal Test for Armyworm. The activities of insecticidal compounds **3f**, **3j**, and **1j** against armyworms were evaluated by foliar application using the reported procedure.[19,20] For the foliar armyworm tests, individual corn leaves were placed on moistened pieces of filter

paper in Petri dishes. The leaves were then dipped in appropriate solutions of the tested compounds for 5 s and exposed to dry. The dishes were infested with 10 third-instar armyworm larvae. Percentage mortalities were evaluated 48 h after treatment.

Insecticidal Test for Aphids. The activities of insecticidal compounds **3f**, **3j**, and **1j** against aphids were tested by the dipping method according to the reported procedure.[20−22] Tender shoots of soybeans with adult aphids were dipped in appropriate solutions of the tested compounds for 5 s. The excess liquid was sucked out with filter paper. Percentage mortalities were evaluated 24 h after treatment.

Insecticidal Test for Carmine Spider Mite. The activities of insecticidal compounds **3i**, **3j**, and **1j** against carmine spider mites were tested by the leaf-dip method according to the reported procedure.[20,23] Horsebean leaves with adult mites were dipped in appropriate solutions of the tested compounds for 5 s. The excess liquid was sucked out with filter paper. Percentage mortalities were evaluated 24 h after treatment.

Photolysis Procedure. Ultraviolet irradiation was carried out at 365 nm with two lamps in an ultraviolet analyzer. About 30 mL of *E-cis*-**1j** (2.85 mmol/L), *cis*-α-cyano-4-fluoro-3-phenoxybenzyl-2,2-dimethyl-3-(2-dichlorovinyl)cyclopropanecarboxylate (**12**) (2.98 mmol/L), and *cis*-α-cyano-4-fluoro-3-phenoxybenzyl-2,2-dimethyl-3-(2-methylpropenyl)cyclopropanecarboxylate (**13**) (2.90 mmol/L) in three quartzose flasks was irradiated for 17 h in hexane. These and a mixture of 0.5 mL of the sample solutions and 0.5 mL of benzyl alcohol in hexane (4 mmol/L) as the internal standard were routinely inspected by GC every hour. At the end of the reaction, inspection by GC-MS followed.[24]

RESULTS AND DISCUSSION

Synthesis. The synthetic procedures for the title compounds are depicted in Scheme 1. Starting from methyl 2,2-dimethyl-3-formylcyclopropanecarboxylate, a set of monohalovinylated acids was synthesized through Wittig reactions. Separation of *cis*-isomers (**8**, **9**) and *trans*-isomers (**10**, **11**) was performed using their different acidities, and the title compounds were obtained by direct esterification of acids and alcohols. The structures of all synthesized compounds were confirmed by ^{1}H NMR.

Bioassay. It has become increasingly clear that the insecticidal activities of pyrethroids are related to their molecular structures, so the insecticidal activities of the synthesized compounds were also tested. Table 1 shows the insecticidal activities of the title compounds against mosquito (*C. pipiens pallens*), a common household pest.

The test results show that the toxic ratio of monohalovinylated pyrethroids was closely related to their molecular structures. First, no obvious difference was observed between monochlorovinylated pyrethroids (**1a**−**c**) and monobromovinylated pyrethroids (**2a**−**c**) with the same alcohol groups. Second, the order of the toxicities of the monohalovinylated pyrethroids with different alcohol groups mosquito was as follows: α-cynao-3-phenoxybenzyl esters (**1c**, **2c**) > polyfluorinatedbenzyl esters (**1f**, **1i**) > allylalcohol esters (**1b**, **2b**) > alkynylalcohol esters (**1a**, **2a**). Third, the toxicities of *cis*-isomers of α-cynao-3-phenoxybenzyl esters (**1c**, **1j**) were higher than those of *trans*-isomers (**3c**, **3j**), whereas those of *cis*-isomers of polyfluorinatedbenzyl esters (**1f**, **1h**) were lower than those of *trans*-isomers (**3f**, **3h**). Fourth, given the same stereostructures, fluorine-containing monohalovinylated pyrethroids had much higher toxicities than those without fluorine (the toxicity of **1j** was about 10 times higher than that of **1c**). Finally, the toxicity of **1j** against mosquito was 2.6 and 22.6 times higher than that of deltamethrin and cypermethrin, respectively.

Table 2. Insecticidal Activities of Compounds 3f, 3j, and 1j against Armyworms (*Mythimna separata*)

concn (mg/L)	**3f** mortality (%)	**3j** mortality (%)	**1j** mortality (%)
50	100	100	100
5	0	100	100
1	0	0	66.7
0.5	0	0	33.3
0.25	nt[a]	nt	0

[a] nt, not tested.

Table 3. Insecticidal Activities of Compounds 1j and Deltamethrin against Armyworms (*Mythimna separata*)

compd	LC_{50} (mg L^{-1})	95% fiducial limit
1j	0.6584	0.5840−0.7423
deltamethrin	0.1486	0.1444−0.1529

Table 4. Insecticidal Activities of Compounds 3f, 3j, and 1j against Aphids (*Aphis craccivora*)

concn (mg/L)	**3f** mortality (%)	**3j** mortality (%)	**1j** mortality (%)
500	100	100	100
50	18.8	100	100
5	0	83.7	89.5
1	0	66.3	84.3
0.5	0	0	28.8
0.25	nt[a]	nt	0

[a] nt, not tested.

On this basis, polyfluorinated benzyl ester (**3f**) and α-cyano-4-fluoro-3-phenoxybenzyl esters (**1j**, **3j**) were selected to further evaluate their activities against armyworms, aphids, and carmine spider mites, three typical agricultural pests. This way, the insecticidal activities of fluorine-containing monohalovinylated pyrethroids could be evaluated comprehensively. Table 2 shows the higher killing activity of **1j** against armyworms; the average mortality rate was 66.7% at 1 mg/L, which is a low concentration. The LC_{50} values of compounds **1j** and decamethrin were 0.1486 and 0.6548 mg/L (Table3), respectively.

Compounds **3j** and **1j** possessed higher insecticidal activities against aphids;, the average mortality rates were 66.3 and 84.3%, respectively, at low concentration (1 mg/L) (Table4). Unexpectedly, compound **1j** demonstrated high insecticidal activity against carmine spider mites; the average mortality rate was 91.1% at 50 mg/L concentration (Table5). Generally, the insecticidal activities of pyrethroids, such as decamethrin and cypermethrin, against mites are weak.[25]

The results of photolysis under UV light at 365 nm indicated that **1j** was easier to degrade than **12** and more difficult to degrade than **13**. These results are in agreement with the theory (Figure 1). After 17 h of treatment, the ratios of *E-cis*-**1j**, **12**, and **13** were 54, 74, and 21%, respectively. The supposed degradation pathway under ultraviolet irradiation was shown in Figure 2, which was similar to that in previous papers.[9,10] The main molecular ion peak detected from GC-MS was obtained from photodegradation of compound **1j** in hexane solution after 17 h. These data support the degradation pathway we supposed in Table 6.

Table 5. Insecticidal Activities of Compounds 3f, 3j, and 1j against Carmine Spider Mites (*Tetranychus cinnabarinus*)

concn (mg/L)	**3f** mortality (%)	**3j** mortality (%)	**1j** mortality (%)
500	0	100	100
50	0	7.8	91.1
5	0	0	11.9
1	0	0	0

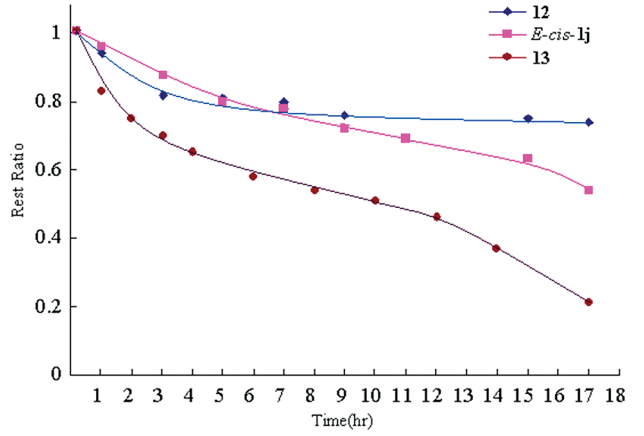


Figure 1. Comparative photodecomposition of **12**, *E-cis*-**1j**, and **13** with similar structures in hexane using UV light.

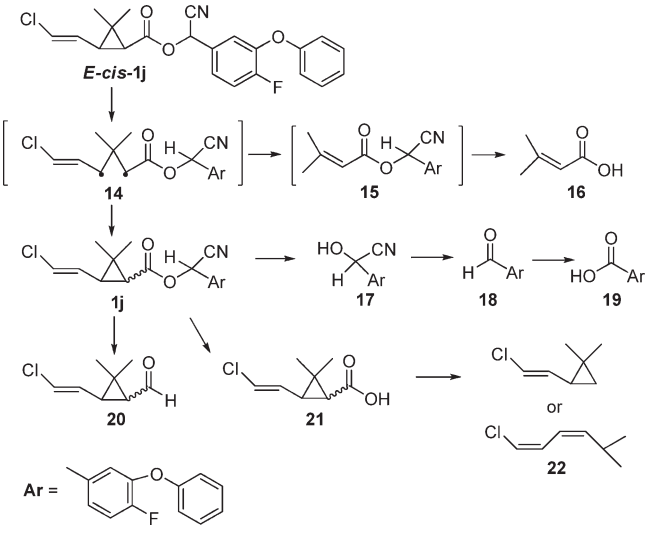


Figure 2. Photochemical pathways for *E-cis*-**1j**. Possible radical intermediates are shown in brackets.

In conclusion, a series of a novel class of pyrethroids, in which one halogen atom was replaced with one hydrogen atom at the double bond, were designed and synthesized. Some of the compounds, such as **3j** and **1j**, which were screened out, had high insecticidal activities against wrigglers, armyworms, and aphids. Such activities were comparable to those of decamethrin and cypermethrin. As well, the synthesized products degraded easily. The atomic economy of compound **1j**, which consisted of a mixture of eight chiral isomers, was much higher than that of decamethrin with fewer isomers; thus, the potential of this compound to improve insecticidal activities by epimerization exists.[26] Monohalovinylated pyrethroid **1j**, which has characteristics of high activity and low residue formation, is a powerful candidate for pesticides. Additional studies on this compound are currently underway.

Table 6. Chromatographic and Spectroscopic Properties of Photoproducts Arising from Ester Cleavage and Other Processes

designation	t_R[a] (min)	MS
16	2.95	100 (M^+)
17	6.87	242 ($[M-1]^+$)
18	6.62	216 ($[M+1]^+$)
19	8.27	232 (M^+)
20	4.05,4.10	157 ($[M-1]^+$)
21	4.69,4.72	174 (M^+)
22	3.03	129 ($[M+1]^+$)

[a] Products arising from E-cis-1j analyzed at 120−300 °C (20 °C/min) by GC-MS.

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