JOC The Journal of Organic Chemistry

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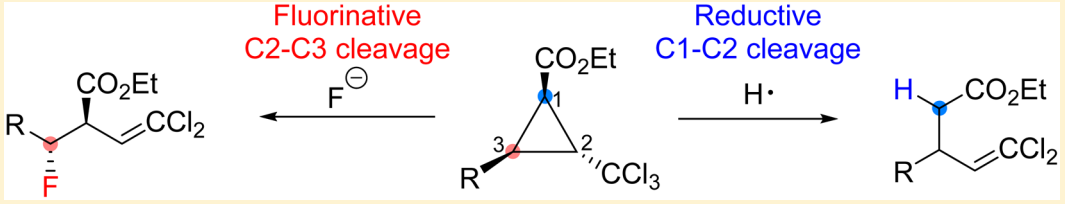
Regiodivergent Ring-Opening Reaction of Trichloromethylcyclopropane Carboxylates

Nobuyoshi Doi, Norihiko Takeda, Okiko Miyata,* and Masafumi Ueda*

Kobe Pharmaceutical University Motoyamakita, Higashinada, Kobe 658-8558, Japan

Supporting Information

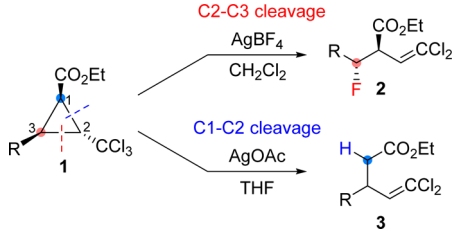


ABSTRACT: Reagent-controlled regiodivergent ring-opening reactions of trichloromethylcyclopropane carboxylates have been developed. The regioselectivity of bond cleavage is completely controlled by the proper choice of silver salts; the treatment of trichloromethylcyclopropane with $AgBF_4$ led to C2−C3 bond cleavage and fluorination to afford fluorinated β,γ-unsaturated ester with high stereoselectivity, while the reaction with AgOAc in THF gave a γ,δ-unsaturated ester through the reductive cleavage of the C1−C2 bond.

INTRODUCTION

Cyclopropanes are highly valuable building blocks in organic synthesis because they readily undergo ring-opening reactions to provide various functionalized compounds.[1−3] Consequently, both the synthesis of a novel cyclopropane bearing a variety of substituents and the development of regioselective ring-opening reactions are attractive and challenging tasks. In particular, controlling the course of the ring-opening of a single substrate with highly tunable selectivity would expand the synthetic utility of cyclopropanes.[2,3] During our studies on the ring-opening reaction of cyclopropane carboxylate **1** bearing a trichloromethyl group,[4] we found that treatment with $AgBF_4$ led to C2−C3 bond cleavage via elimination of a chloride anion to afford fluorinated β,γ-unsaturated ester **2** with high stereoselectivity, while the reaction with AgOAc in THF gave γ,δ-unsaturated ester **3** through the cleavage of the C1−C2 bond (Scheme 1). Owing to their simplicity, convenience, and high selectivity, both tunable regioselective ring-opening reactions provide a new route to highly functionalized alkenes. It is noteworthy that these unconjugated esters would otherwise be difficult to prepare using conventional synthetic methods. Herein, we report in detail the reagent-controlled regiodivergent ring-opening reactions of trichloromethylcyclopropane carboxylates.

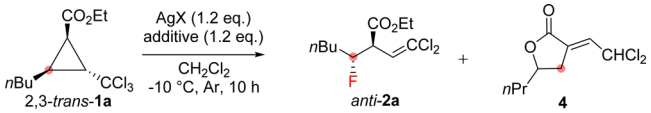
Scheme 1. Regiodivergent Ring-Opening Reaction of Trichloromethylcyclopropane Carboxylate 1



RESULTS AND DISCUSSION

We began our study on the ring-opening fluorination of trichloromethylcyclopropanes **1** with silver salts that have high affinity for the chlorine atom (Table 1).[5−8] When 2,3-*trans*-**1a** was treated with $AgBF_4$ in CH_2Cl_2 at −10 °C, the expected ring-opening and fluorination produced fluorinated product *anti*-**2a** as a single stereoisomer in 60% yield along with lactone

Table 1. Optimization of the Ring-Opening Fluorination



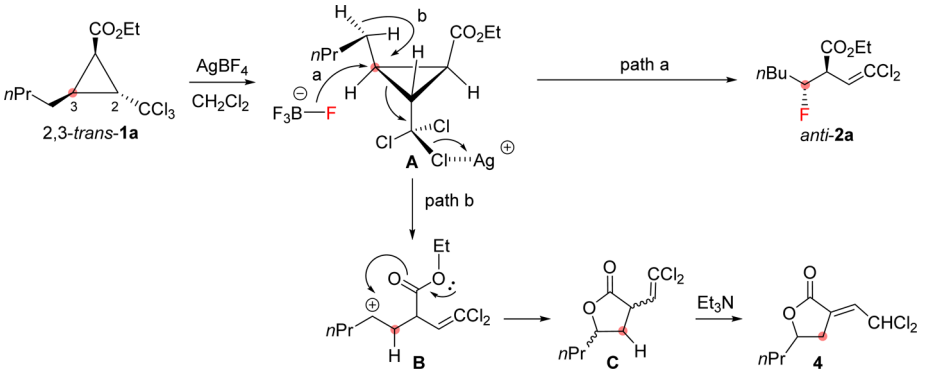
entry	AgX	additive	yield (%)[a] *anti*-**2a**	yield (%)[a] **4**[b]
1	$AgBF_4$	–	60	5
2	$AgPF_6$	–	trace	32
3	$AgSbF_6$	–	– (19)	43
4	$AgBF_4$	KF	59 (10)	7
5	$AgBF_4$	$LiBF_4$	64	8
6	$AgBF_4$	Bu_4NBF_4	81	–

[a]Yields in parentheses are for recovered starting material. [b]Lactone **4** was exclusively obtained after the treatment of the mixture of **4** and its double-bond regioisomer with Et_3N.

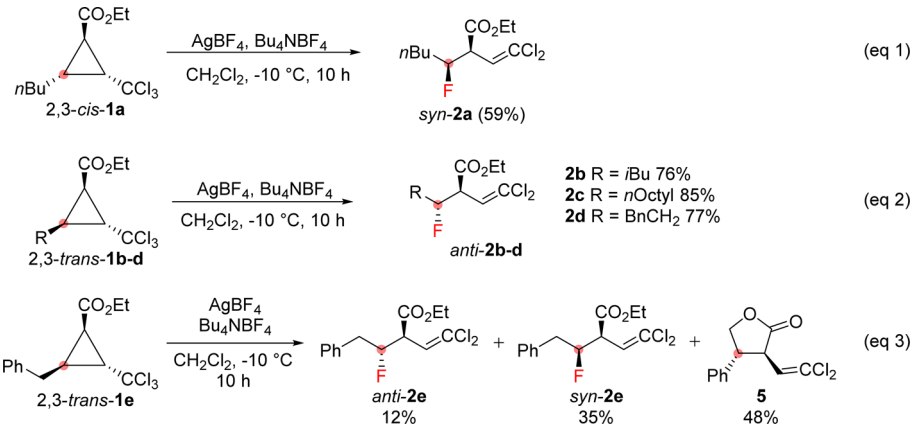
Received: June 23, 2016
Published: August 3, 2016

DOI: 10.1021/acs.joc.6b01508
J. Org. Chem. 2016, 81, 7855−7861

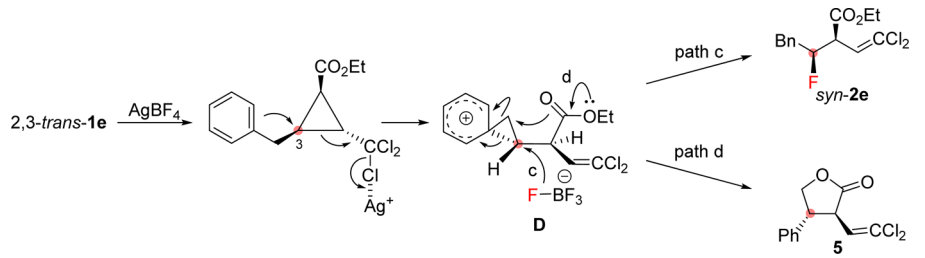
Scheme 2. Possible Reaction Pathway of the Ring-Opening Fluorination Reaction



Scheme 3. Stereochemistry and Substituent Effects of Ring-Opening Fluorination



Scheme 4. Possible Reaction Pathway via the Phenonium Ion Intermediate of 1e



4 in 5% yield (entry 1). Other silver reagents, $AgPF_6$ or $AgSbF_6$, did not give fluorinated product **2a**,[9] while lactone **4** was obtained as a major product (entries 2 and 3). Examination of additives revealed that Bu_4NBF_4 dramatically improved the chemical yield of the desired product **2a**. Indeed, the reaction with $AgBF_4$ (1.2 equiv) and Bu_4NBF_4 (1.2 equiv) in CH_2Cl_2 at −10 °C proceeded effectively to give *anti*-**2a** in 81% yield (entry 6).

A possible reaction pathway is shown in Scheme 2. A chlorine atom of the trichloromethyl group would coordinate to Ag(I). Subsequently, fluoride transfer from tetrafluoroborate to C3,[10] cleavage of the C2−C3 bond, and elimination of the silver-activated chlorine atom occur in an S_N2' manner to afford the inverted product *anti*-**2a** (path a). On the other hand, lactone **4** would be formed through 1,2-hydrogen shift-triggered ring-opening followed by cyclization of carbocation intermediate **B** (path b).

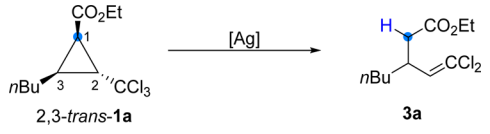
With the optimized conditions in hand, we investigated the ring-opening fluorination of different cyclopropanes by varying the stereostructure and C3 substituent (Scheme 3). The reaction of 2,3-*cis*-**1a** with $AgBF_4$ predominately gave *syn*-**2a**, indicating that this reaction is stereospecific (eq 1). Other substituents at C3, such as branched and linear alkyl chains and the phenethyl group, were readily accommodated, producing the expected fluorinated alkenes *anti*-**2b−d** (eq 2). In marked contrast, trichloromethylcyclopropane **1e** bearing a benzyl group was treated with $AgBF_4$ and Bu_4NBF_4, the expected *anti*-**2e** was a minor product, and *syn*-**2e** and lactone **5** were obtained in 35% and 48% yields, respectively (eq 3). *syn*-**2e** and **5** could be formed via the generation of phenonium ion intermediate **D** by intramolecular nucleophilic attack of the phenyl group onto the C3 position (Scheme 4).[11−13]

Based on the above results, we envisaged that the reaction of trichloromethylcyclopropane carboxylates **1** with silver acetate, which lacks a nucleophilic fluorine atom, would lead to selective formation of lactones **4**. Treatment of 2,3-*trans*-**1a** with AgOAc in CH_2Cl_2 or THF at room temperature, however, did not afford the desired lactone, and starting material **1a** was

DOI: 10.1021/acs.joc.6b01508
J. Org. Chem. 2016, 81, 7855−7861

completely recovered (Table 2, entries 1 and 2). Surprisingly, the reaction with AgOAc in refluxing THF did give γ,δ-

Table 2. Optimization of the Reductive Ring-Opening Reaction



2,3-*trans*-**1a** → **3a**

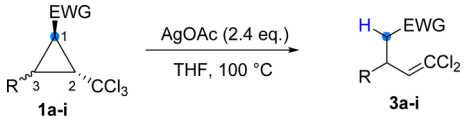
entry	Ag(I) (equiv)	solvent	*T* (°C)	yield (%)[b]
1	AgOAc (2.4)	CH_2Cl_2	rt	NR
2	AgOAc (2.4)	THF	rt	NR
3	AgOAc (2.4)	THF	reflux	25 (36)
4[a]	AgOAc (2.4)	THF	100	82
5[a]	AgCN (2.4)	THF	100	51 (39)
6[a]	Ag_2O (1.2)	THF	100	26 (54)
7[a]	AgF (2.4)	THF	100	68

[a]The reactions were performed in a sealed tube for 18−24 h. [b]Yields in parentheses are for the recovered starting material.

unsaturated ester **3a** in 25% yield (entry 3). It should be noted that **3a** was formed via cleavage of the C1−C2 bond followed by reduction, which is in contrast to the reaction with $AgBF_4$. Increasing the reaction temperature to 100 °C improved the chemical yield to 82% (entry 4). The survey of other Ag(I) reagents revealed that AgOAc is superior to other reagents such as AgCN and Ag_2O (entries 5 and 6). Interestingly, although AgF bears a nucleophilic fluorine atom, the reductive ring-opening reaction predominately proceeded to afford **3a** in 68% yield (entry 7).

These interesting results led us to investigate the generality of the reductive ring-opening reaction and clarify the reaction mechanism (Table 3). The effects of different substituents on

Table 3. Substituent Effects of the Reductive Ring-Opening Reaction[a]



1a-i → **3a-i**

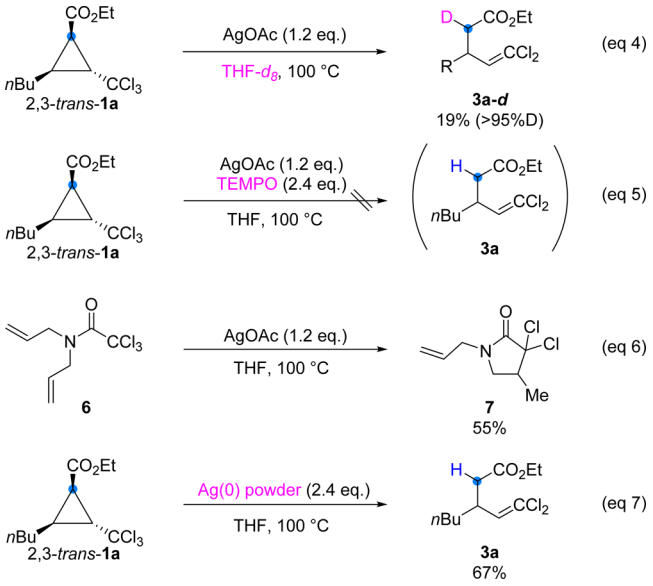
entry	substrate	EWG	R	yield (%)
1	2,3-*trans*-**1b**	CO_2Et	*i*Bu	81
2	2,3-*trans*-**1c**	CO_2Et	*n*Octyl	76
3	2,3-*trans*-**1f**	CO_2Et	*t*Bu	80
4	2,3-*trans*-**1g**	CO_2Et	cyclopentyl	88
5	2,3-*trans*-**1e**	CO_2Et	Bn	56
6	2,3-*trans*-**1h**	CON(OMe)Me	*n*Bu	74
7	2,3-*trans*-**1i**	CN	*n*Bu	84
8	2,3-*cis*-**1a**	CO_2Et	*n*Bu	84

[a]The reactions were performed in a sealed tube for 24 h.

the cyclopropane ring were examined. Substrates 2,3-*trans*-**1b**−**g**, which possess various alkyl groups at the C3 position, underwent facile ring-opening and gave γ,δ-unsaturated esters **3b**−**g** in moderate to good yields (entries 1−5). Variations in the electron-withdrawing substituents at the C1 position, such as a Weinreb amide and a nitrile, were also tolerated (entries 6 and 7). The stereochemistry of the substrate did not affect the course of the reaction; thus, 2,3-*cis*-**1a** gave **3a** in 84% yield (entry 8).

To gain an understanding of the reaction mechanism, control experiments were conducted (Scheme 5). To elucidate the

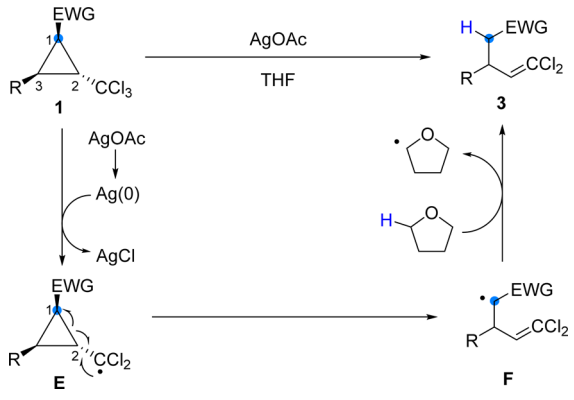
Scheme 5. Control Experiments for Determining the Mechanism of the Reductive Ring-Opening Reaction



hydrogen source of the α-position in **3**, a deuterium-labeling study was carried out (eq 4). When **1a** was treated with AgOAc in THF-d_8, deuterated product **3a-*d*** was obtained. In addition, no reaction occurred in the presence of TEMPO as a radical scavenger (eq 5). These results suggest that the newly discovered reductive ring-opening reaction might proceed through a radical process. To confirm the generation of radical species, the radical cyclization of trichloroacetamide **6**[14] was carried out under AgOAc-mediated reaction conditions in THF (eq 6). As a result, cyclized product **7** was obtained in 55% yield. To determine the real radical initiator for this reaction, reaction with Ag(0) powder was conducted (eq 7). Expectedly, acyclic product **3a** was obtained, indicating that the Ag(I) in the previous examples was reduced to Ag(0), which would act as a radical initiator in the AgOAc-mediated reaction.

On the basis of the above experimental observations, a reaction pathway is postulated (Scheme 6). Ag(0) is first generated from silver acetate.[15] Zero-valent silver then abstracts a chlorine atom from the trichloromethyl group to generate

Scheme 6. Possible Reaction Pathway of the Reductive Ring-Opening Reaction

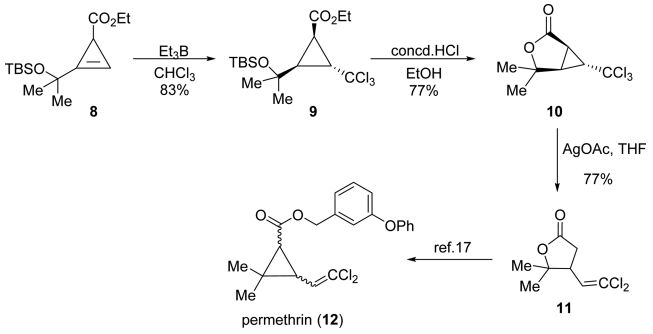


DOI: 10.1021/acs.joc.6b01508
J. Org. Chem. 2016, 81, 7855−7861

dichloromethyl radical **E**,[16] which undergoes C1−C2 bond cleavage to form stabilized α-carbonyl radical **F**. Finally, **F** abstracts a hydrogen atom from THF to give **3**.[17]

The applicability of the protocol was further demonstrated in the synthesis of dichloroalkene **11**, which is a key intermediate in the synthesis of insecticide permethrin (**12**) (Scheme 7).[18,19]

Scheme 7. Formal Synthesis of Permethrin



The triethylborane-mediated trichloromethylation[4] of cyclopropene **8** gave trichloromethylcyclopropane **9**, which underwent lactonization by treatment with concd. HCl to afford bicyclic compound **10**. Finally, the reductive ring-opening reaction of **10** with AgOAc in THF furnished dichloroalkenyllactone **11** in good yield.

CONCLUSION

In conclusion, we have developed a novel regiodivergent Ag(I)-mediated ring-opening reaction of cyclopropanes bearing the trichloromethyl group. The regioselectivity of bond cleavage is completely controlled by the proper choice of silver salts, and both the fluorinated β,γ-unsaturated and γ,δ-unsaturated esters can be prepared from a single substrate.

EXPERIMENTAL SECTION

General Infomation. Infrared (IR) spectra were recorded on film as absorption wavenumbers (cm^{-1}). ^1H NMR spectra were recorded at ambient temperature on a 300, 500, 600 MHz FT-NMR spectrometer. Chemical shifts are reported in parts per million from tetramethylsilane (0.00 ppm) resonance as the internal standard. Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet, br = broad), and coupling constants (Hz). ^{13}C NMR spectra were recorded at ambient temperature on a 75, 125, 150 MHz FT-NMR spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from the solvent resonance as the internal standard ($CDCl_3$; 77.00 ppm). The high-resolution mass spectra (HRMS) were conducted on an FT-ESI mass analyzer. Preparative TLC separations (PTLC) were carried out on precoated silica gel plates (E. Merck 60F254). Medium-pressure column chromatography was performed using Lobar größe B (E. Merck 310−25, Lichroprep Si60). Unless otherwise stated, all the reagents and solvents were used as received from the manufacturer.

Trichloromethylcyclopropane carboxlates **1a−g**[4] and trichloroacetamide **6**[20] were prepared according to literature procedures.

General Procedure for Preparation of Trichloromethylcyclopropane Carboxylates. The following procedure for the trichloromethylation of 2-butyl-*N*-methoxy-*N*-methyl-2-cyclopropene-1-carboxamide is representative. To a solution of 2-butyl-*N*-methoxy-*N*-methyl-2-cyclopropene-1-carboxamide (50.0 mg, 0.27 mmol) in $CHCl_3$ (2.7 mL) was added Et_3B (1.0 M in hexane, 0.27 mL, 0.27 mmol) under nitrogen atmosphere at rt. After being stirred at the same temperature for 2 h, the reaction mixture was concentrated at reduced pressure. The crude product was purified by medium-pressure column chromatography (hexane:AcOEt = 10:1) to afford the corresponding cyclopropanes **1h** (40.7 mg, 49%).

*1,2-trans-2,3-trans-3-Butyl-N-methoxy-N-methyl-2-(trichloromethyl)cyclopropane-1-carboxamide (**1h**).* A colorless oil (40.7 mg, 49% yield). IR (neat): 1660 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ: 3.77 (s, 3H), 3.23 (s, 3H), 2.83 (dd, J_{HH} = 6.0, 5.0 Hz, 1H), 2.78−2.70 (brs, 1H), 1.95−1.85 (m, 1H), 1.61−1.53 (m, 2H), 1.47−1.25 (m, 4H), 0.89 (t, J_{HH} = 7.0 Hz, 3H) ^{13}C NMR (75 MHz, $CDCl_3$) δ: 169.1, 98.9, 61.6, 44.8, 32.6, 31.4, 29.7, 25.3, 25.1, 22.3, 14.1. HRMS (ESI) *m/z*: Calcd for $C_{11}H_{18}NO_2{}^{35}Cl_3Na$ $[M + Na]^+$ 324.0295. Found: 324.0295.

*1,2-trans-2,3-trans-3-Butyl-2-(trichloromethyl)cyclopropane-1-carbonitrile (**1i**).* A colorless oil (487.6 mg, 51% yield). IR (neat): 2244 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ: 2.50 (t, J_{HH} = 5.0 Hz, 1H), 2.10 (dd, J_{HH} = 9.0, 5.0 Hz, 1H), 1.89−1.36 (m, 7H), 0.94 (t, J_{HH} = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 117.2, 96.4, 45.5, 30.4, 28.6, 26.4, 22.2, 13.9, 11.5. HRMS (ESI) *m/z*: Calcd for $C_9H_{12}N^{35}Cl_3Na$ $[M + Na]^+$ 261.9928. Found: 261.9929.

*anti-2-(2,2-Dichloroethenyl)-3-fluoroheptanoic Acid Ethyl Ester (anti-**2a**).* A two-neck flask was charged with $AgBF_4$ (42.0 mg, 0.21 mmol) and Bu_4NBF_4 (71.1 mg, 0.21 mmol) in a glovebox at nitrogen atmosphere, evacuated, and backfilled with argon. Dichloromethane (3 mL) was added to this flask, and the mixture was stirred at −10 °C. A solution of 2,3-*trans*-**1a** (52.6 mg, 0.18 mmol) in dichloromethane (3 mL) was added to this mixture and stirring continued for 10 h at −10 °C. Then the reaction mixture was diluted with H_2O and filtered through a thin pad of Celite. The filtrate was extracted with $CHCl_3$, and the organic layer was dried over $MgSO_4$ and concentrated at reduced pressure. The residue was purified by preparative TLC (hexane: AcOEt = 10:1) to afford *anti*-**2a** (39.3 mg, 81%).

A colorless oil (39.3 mg, 81%). IR (neat) 1739 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ: 6.10 (d, J_{HH} = 10.0 Hz, 1H), 4.93 (ddt, $^2J_{HF}$ = 48.0, J_{HH} = 9.0, 3.5 Hz, 1H), 4.22 (q, J_{HH} = 7.0 Hz, 2H), 3.57 (ddd, $^3J_{HF}$ = 28.0, J_{HH} = 10.0, 3.5 Hz, 1H), 1.76−1.28 (m, 6H), 1.29 (t, J_{HH} = 7.0 Hz, 3H), 0.92 (t, J_{HH} = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 169.3 (d, $^3J_{CF}$ = 4.0 Hz), 124.6, 122.7, 93.2, 61.7, 51.2 (d, $^2J_{CF}$ = 22.0 Hz), 32.4 (d, $^2J_{CF}$ = 20.0 Hz), 27.2 (d, $^3J_{CF}$ = 4.0 Hz), 22.3, 14.1, 13.9. HRMS (ESI) *m/z*: Calcd for $C_{11}H_{17}O_2F^{35}Cl_2Na$ $[M + Na]^+$ 293.0482. Found: 293.0477.

The stereostructure was deduced on the basis of the larger vicinal HF coupling constant than that of the other isomer *syn*-**2a**.[21]

*(E)-3-(2,2-Dichloroethylidene)-dihydro-5-propyl-2(3H)-furanone (**4**).* A two-neck flask was charged with $AgSbF_6$ (74.2 mg, 0.21 mmol) in a glovebox at nitrogen atomosphere, evacuated, and backfilled with argon. Dichloromethane (3 mL) was added to this flask, and the mixture was stirred at −10 °C. A solution of 2,3-*trans*-**1a** (52.6 mg, 0.18 mmol) in dichloromethane (3 mL) was added to this mixture and stirring continued for 10 h at −10 °C. Then the reaction mixture was diluted with H_2O and filtered through a thin pad of Celite. The filtrate was extracted with $CHCl_3$, and the organic layer was dried over $MgSO_4$ and concentrated at reduced pressure. To a solution of the crude product in dichloromethane (1 mL) was added Et_3N (42 μL, 0.3 mmol) under nitrogen atmosphere at rt. After being stirred at the same temperature for 24 h, the reaction mixture was extracted with $CHCl_3$. The organic layer was dried over $MgSO_4$, and the solvents were removed under vacuum. The residue was purified by preparative TLC (hexane: AcOEt = 10:1) to afford lactone **4** (17.4 mg, 43%).

A colorless oil (17.4 mg. 43% yield). IR (neat) 1761 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ: 6.90 (dt, J_{HH} = 9.0, 3.0 Hz, 1H), 6.24 (d, J_{HH} = 9.0 Hz, 1H), 4.62 (tt, J_{HH} = 7.5, 6.0 Hz, 1H), 3.14 (ddd, J_{HH} = 18.0, 7.5, 3.0 Hz, 1H), 2.62 (ddd, J_{HH} = 18.0, 6.0, 3.0 Hz, 1H), 1.82−1.38 (m, 4H), 0.98 (t, J_{HH} = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 169.4, 134.5, 128.7, 77.9, 66.0, 38.4, 31.1, 18.1, 13.7. HRMS (ESI) *m/z*: Calcd for $C_9H_{13}{}^{35}Cl_2O_2$ $[M + H]^+$ 223.0287. Found: 223.0292.

*syn-2-(2,2-Dichloroethenyl)-3-fluoroheptanoic Acid Ethyl Ester (syn-**2a**).* A two-neck flask was charged with $AgBF_4$ (42.0 mg, 0.21 mmol) and Bu_4NBF_4 (71.1 mg, 0.21 mmol) in a glovebox at nitrogen atmosphere, evacuated, and backfilled with argon. Dichloromethane (3 mL) was added to this flask, and the mixture was stirred at −10 °C. A solution of 2,3-*cis*-**1a** (52.6 mg, 0.18 mmol) in dichloromethane (3

DOI: 10.1021/acs.joc.6b01508
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mL) was added to this mixture and stirring continued for 10 h at −10 °C. Then the reaction mixture was diluted with H_2O and filtered through a thin pad of Celite. The filtrate was extracted with $CHCl_3$, and the organic layer was dried over $MgSO_4$ and concentrated at reduced pressure. The residue was purified by preparative TLC (hexane: AcOEt = 10:1) to afford *syn*-**2a** (29.0 mg, 59%).

A colorless oil (29.0 mg. 59% yield). IR (neat) 1743 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ: 5.97 (d, J_{HH} = 10.0 Hz, 1H), 4.72 (dtd, $^2J_{HF}$ = 47.0 Hz, J_{HH} = 7.5, 5.0 Hz, 1H), 4.20 (qd, J_{HH} = 7.0, 2.5 Hz, 2H), 3.71 (ddd, $^3J_{HF}$ = 12.0 Hz, J_{HH} = 10.0, 7.5 Hz, 1H), 1.72−1.22 (m, 6H), 1.29 (t, J_{HH} = 7.0 Hz, 3H), 0.92 (t, J_{HH} = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 169.1 (d, $^3J_{CF}$ = 4.0 Hz), 124.9, 123.1 (d, $^3J_{CF}$ = 8.5 Hz), 93.2 (d, $^1J_{CF}$ = 175.0 Hz), 61.6, 51.9 (d, $^2J_{CF}$ = 24.0 Hz), 32.2 (d, $^2J_{CF}$ = 20.0 Hz), 27.1 (d, $^3J_{CF}$ = 3.0 Hz), 22.3, 14.1, 13.9. HRMS (ESI) *m*/*z*: Calcd for $C_{11}H_{17}{}^{35}Cl_2FO_2Na$ $[M + Na]^+$ 293.0482. Found: 293.0477.

The stereostructure was deduced on the basis of the smaller vicinal HF coupling constant than that of the other isomer *anti*-**2a**.[21]

General Procedure for $AgBF_4$-Mediated Fluorination/Ring-opening Reaction of Cyclopropane Bearing Trichloromethyl Group. The following procedure for the fluorination/ring-opening reaction of 2,3-*trans*-**1b** is representative. A two-neck flask was charged with $AgBF_4$ (42.0 mg, 0.21 mmol) and Bu_4NBF_4 (71.1 mg, 0.21 mmol) in a glovebox at nitrogen atmosphere, evacuated, and backfilled with argon. Dichloromethane (3 mL) was added to this flask, and the mixture was stirred at −10 °C. A solution of 2,3-*trans*-**1b** (52.6 mg, 0.18 mmol) in dichloromethane (3 mL) was added to this mixture and stirring continued for 10 h at −10 °C. Then the reaction mixture was diluted with H_2O and filtered through a thin pad of Celite. The filtrate was extracted with $CHCl_3$, and the organic layer was dried over $MgSO_4$ and concentrated at reduced pressure. The residue was purified by preparative TLC (hexane: AcOEt = 10:1) to afford *anti*-**2b** (37.2 mg, 76%).

*anti-2-(2,2-Dichloroethenyl)-3-fluoro-5-methylhexanoic Acid Ethyl Ester (anti-**2b**).* A colorless oil (37.2 mg, 76% yield). IR (neat) 1740 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ: 6.10 (d, J_{HH} = 10.0 Hz, 1H), 5.03 (ddt, $^2J_{HF}$ = 48.0 Hz, J_{HH} = 10.0, 3.5 Hz, 1H), 4.22 (q, J_{HH} = 7.0 Hz, 2H), 3.54 (ddd, $^3J_{HF}$ = 28.0 Hz, J_{HH} = 10.0, 3.5 Hz, 1H), 1.87−1.59 (m, 2H), 1.37−1.17 (m, 1H), 1.30 (t, J_{HH} = 7.0 Hz, 3H), 0.96 (d, J_{HH} = 6.5 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 169.3 (d, $^3J_{CF}$ = 4.0 Hz), 124.6, 122.7 (d, $^3J_{CF}$ = 4.5 Hz), 91.7 (d, $^1J_{CF}$ = 176.0 Hz), 61.7, 51.5 (d, $^2J_{CF}$ = 22.0 Hz), 41.5 (d, $^2J_{CF}$ = 20.0 Hz), 24.5 (d, $^3J_{CF}$ = 3.5 Hz), 23.1, 21.9, 14.1. HRMS (ESI) *m*/*z*: Calcd for $C_{11}H_{17}{}^{35}Cl_2FO_2Na$ $[M + Na]^+$ 293.0482. Found: 293.0485.

The stereostructure was deduced by the similarity of vicinal HF coupling constants with *anti*-**2a**.

*anti-2-(2,2-Dichloroethenyl)-3-fluoroundecanoic Acid Ethyl Ester (anti-**2c**).* A colorless oil (50.1 mg, 85% yield). IR (neat) 1740 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ: 6.10 (d, J_{HH} = 10.0 Hz, 1H), 4.93 (ddt, $^2J_{HF}$ = 48.0 Hz, J_{HH} = 8.5, 4.0 Hz, 1H), 4.22 (q, J_{HH} = 7.0 Hz, 2H), 3.57 (ddd, $^3J_{HF}$ = 28.0 Hz, J_{HH} = 10.0, 4.0 Hz, 1H), 1.74−1.21 (m, 14H), 1.29 (t, J_{HH} = 7.0 Hz, 3H), 0.88 (t, J_{HH} = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 169.3 (d, $^3J_{CF}$ = 4.0 Hz), 124.6, 122.7 (d, $^3J_{CF}$ = 4.5 Hz), 93.2 (d, $^1J_{CF}$ = 176.0 Hz), 61.7, 57.1 (d, $^2J_{CF}$ = 21.0 Hz), 32.7 (d, $^2J_{CF}$ = 20.0 Hz), 31.8, 29.4, 29.2, 29.1, 25.0 (d, $^3J_{CF}$ = 4.5 Hz), 22.6, 14.1. HRMS (ESI) *m*/*z*: Calcd for $C_{15}H_{25}{}^{35}Cl\ {}_2FO_2Na$ $[M + Na]^+$ 349.1108. Found: 349.1107.

The stereostructure was deduced by the similarity of vicinal HF coupling constants with *anti*-**2a**.

*anti-2-(2,2-Dichloroethenyl)-3-fluoro-5-phenylpentanoic Acid Ethyl Ester (anti-**2d**).* A colorless oil (44.1 mg, 77% yield). IR (neat) 1738 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ: 7.35−7.16 (m, 5H), 6.11 (d, J_{HH} = 10.0 Hz, 1H), 4.95 (ddt, $^2J_{HF}$ = 48.0 Hz, J_{HH} = 9.5, 3.5 Hz, 1H), 4.21 (q, J_{HH} = 7.0 Hz, 2H), 3.59 (ddd, $^3J_{HF}$ = 27.5 Hz, J_{HH} = 10.0, 3.5 Hz, 1H), 2.96−2.64 (m, 2H), 2.13−1.94 (m, 2H), 1.28 (t, J_{HH} = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 169.1 (d, $^3J_{CF}$ = 4.0 Hz), 140.5, 128.6, 128.4, 126.3, 124.9, 122.6 (d, $^3J_{CF}$ = 4.5 Hz), 92.2 (d, $^1J_{CF}$ = 177.0 Hz), 61.8, 51.1 (d, $^2J_{CF}$ = 21.0 Hz), 34.6 (d, $^2J_{CF}$ = 20.0 Hz), 31.3 (d, $^3J_{CF}$ = 4.5 Hz), 14.1. HRMS (ESI) *m*/*z*: Calcd for $C_{15}H_{18}{}^{35}Cl_2FO_2$ $[M + H]^+$ 319.0662. Found: 319.0657.

The stereostructure was deduced by the similarity of vicinal HF coupling constants with *anti*-**2a**.

*$AgBF_4$-Mediated Fluorination/Ring-Opening Reaction of Trichloromethylcyclopropane Carboxylate **1e**.* A two-neck flask was charged with $AgBF_4$ (42.0 mg, 0.21 mmol) and Bu_4NBF_4 (71.1 mg, 0.21 mmol) in a glovebox at nitrogen atmosphere, evacuated, and backfilled with argon. Dichloromethane (3 mL) was added to this flask, and the mixture was stirred at −10 °C. A solution of 2,3-*trans*-**1e** (57.9 mg, 0.18 mmol) in dichloromethane (3 mL) was added to this mixture and stirring continued for 10 h at −10 °C. Then the reaction mixture was diluted with H_2O and filtered through a thin pad of Celite. The filtrate was extracted with $CHCl_3$, and the organic layer was dried over $MgSO_4$ and concentrated at reduced pressure. The residue was purified by preparative TLC (hexane:AcOEt = 10:1) to afford the mixture *anti*-**2e** and *syn*-**2e** (25.8 mg, 47%, *anti*:*syn* = 1:3) and lactone **5** (22.2 mg, 48%).

*anti-4,4-dichloro-2-(1-fluoro-2-phenylethyl)-3-butenoic Acid Ethyl Ester (anti-**2e**).* A colorless oil. IR (neat) 1738 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ: 7.36−7.21 (m, 5H), 6.16 (d, J_{HH} = 10.0 Hz, 1H), 5.18 (dddd, $^2J_{HF}$ = 47.0 Hz, J_{HH} = 8.0, 5.0, 3.5 Hz, 1H), 4.20 (q, J_{HH} = 7.0 Hz, 2H), 3.60 (ddd, $^3J_{HF}$ = 28.0 Hz, J_{HH} = 10.0, 3.5 Hz, 1H), 3.04 (td, J_{HH} = 14.5, 8.0 Hz, 1H), 2.84 (ddd, $^3J_{HF}$ = 28.0 Hz, J_{HH} = 14.5, 5.0 Hz, 1H), 1.28 (t, J_{HH} = 7.0 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 169.1 (d, $^3J_{CF}$ = 4.0 Hz), 135.7 (d, $^3J_{CF}$ = 5.0 Hz), 129.3, 128.7, 127.1, 125.3, 122.3 (d, $^3J_{CF}$ = 4.5 Hz), 93.3 (d, $^1J_{CF}$ = 179.0 Hz), 61.8, 50.6 (d, $^2J_{CF}$ = 21.0 Hz), 39.2 (d, $^2J_{CF}$ = 22.0 Hz), 14.1. HRMS (ESI) *m*/*z*: Calcd for $C_{14}H_{16}{}^{35}Cl_2FO_2$ $[M + H]^+$ 305.0506. Found: 305.0501.

The stereostructure was deduced on the basis of the larger vicinal HF coupling constant than that of the other isomer *syn*-**2e**.[21]

*syn-4,4-dichloro-2-(1-fluoro-2-phenylethyl)-3-butenoic Acid Ethyl Ester (syn-**2e**).* A colorless oil. IR (neat) 1738 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ: 7.33−7.20 (m, 5H), 6.00 (d, J_{HH} = 10.0 Hz, 1H), 4.93 (dtd, $^2J_{HF}$ = 47.0 Hz, J_{HH} = 7.0, 5.0 Hz, 1H), 4.20 (q, J_{HH} = 7.0 Hz, 2H), 3.74 (ddd, $^3J_{HF}$ = 13.0 Hz, J_{HH} = 10.0, 7.0 Hz, 1H), 3.06−2.92 (m, 2H), 1.28 (t, J_{HH} = 7.0 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 168.8 (d, $^3J_{CF}$ = 4.5 Hz), 136.0 (d, $^3J_{CF}$ = 2.5 Hz), 129.4, 128.6, 127.0, 125.3, 122.9 (d, $^3J_{CF}$ = 8.0 Hz), 93.5 (d, $^1J_{CF}$ = 180.0 Hz), 61.7, 51.4 (d, $^2J_{CF}$ = 24.0 Hz), 38.9 (d, $^2J_{CF}$ = 21.0 Hz), 14.1. HRMS (ESI) *m*/*z*: Calcd for $C_{14}H_{16}{}^{35}Cl_2FO_2$ $[M + H]^+$ 305.0506. Found: 305.0504.

The stereostructure was deduced on the basis of the smaller vicinal HF coupling constant than that of the other isomer *anti*-**2e**.[21]

(3R,4R*)-3-(2,2-Dichloroethenyl)dihydro-4-pheny-2(3H)-furanone (**5**).* White crystals (22.2 mg, 48% yield). Mp: 102−103 °C (hexane-AcOEt). IR ($CHCl_3$) 1770 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ: 7.43−7.26 (m, 5H), 5.86 (d, J_{HH} = 9.5 Hz, 1H), 4.64 (dd, J_{HH} = 9.0, 8.0 Hz, 1H), 4.26 (dd, J_{HH} = 11.0, 9.0 Hz, 1H), 3.88 (dd, J_{HH} = 11.0, 9.5 Hz, 1H), 3.63 (td, J_{HH} = 11.0, 8.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 173.8, 135.8, 129.3, 128.3, 127.2, 123.3, 72.0, 48.5, 48.2. HRMS (ESI) *m*/*z*: Calcd for $C_{12}H_{10}{}^{35}Cl_2O_2Na$ $[M + Na]^+$ 278.9950. Found: 278.9949.

General Procedure for AgOAc-Mediated Reductive Ring-opening Reaction of Cyclopropane. The following procedure for the reductive ring-opening reaction of 2,3-*trans*-**1a** is representative. A solution of 2,3-*trans*-**1a** (50.0 mg, 0.17 mmol) and AgOAc (34.9 mg, 0.2 mmol) in THF (5 mL) was added to a sealed tube. After being stirred at 100 °C for 24 h, the reaction mixture was filtered through a thin pad of Celite. The filtrate was concentrated at reduced pressure. The residue was purified by preparative TLC (hexane:AcOEt = 10:1) to afford **3a** (36.2 mg, 82%).

*Ethyl 3-(2,2-Dichloroethenyl)heptanoate (**3a**).* A colorless oil (36.2 mg, 82% yield). IR (neat) 1737 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ: 5.70 (d, J_{HH} = 10.0 Hz, 1H), 4.14 (qd, J_{HH} = 7.0, 1.0 Hz, 2H), 2.97−2.89 (m, 1H), 2.40 (dd, J_{HH} = 15.0, 6.0 Hz, 1H), 2.29 (dd, J_{HH} = 15.0, 7.5 Hz, 1H), 1.50−1.44 (m, 1H), 1.40−1.23 (m, 5H), 1.26 (t, J_{HH} = 7.0 Hz, 3H), 0.89 (t, J_{HH} = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 171.6, 132.6, 120.9, 60.5, 39.3, 37.2, 34.0, 29.1, 22.6, 14.2, 13.9. HRMS (ESI) *m*/*z*: Calcd for $C_{11}H_{19}O_2{}^{35}Cl_2$ $[M + H]^+$ 253.0757. Found: 253.0754.

DOI: 10.1021/acs.joc.6b01508
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*Ethyl 3-(2,2-Dichloroethenyl)-5-methylhexanoate (**3b**).* A colorless oil (35.5 mg, 81% yield). IR (neat) 1737 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ: 5.68 (d, J_{HH} = 10.0 Hz, 1H), 4.21−4.07 (m, 2H), 3.09−2.96 (m, 1H), 2.38 (dd, J_{HH} = 15.0, 6.0 Hz, 1H), 2.27 (dd, J_{HH} = 15.0, 7.5 Hz, 1H), 1.62−1.48 (m, 1H), 1.35−1.19 (m, 2H), 1.27 (t, J_{HH} = 7.0 Hz, 3H), 0.92 (d, J_{HH} = 6.5 Hz, 3H), 0.90 (d, J_{HH} = 6.5 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 171.6, 132.7, 120.7, 60.5, 43.6, 39.6, 35.4, 25.7, 23.2, 22.0, 14.2. HRMS (ESI) *m/z*: Calcd for $C_{11}H_{18}O_2{}^{35}Cl_2Na$ $[M + Na]^+$ 275.0576. Found: 275.0577.

*Ethyl 3-(2,2-Dichloroethenyl)undecanoate (**3c**).* A colorless oil (40.8 mg, 76% yield). IR (neat) 1737 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ: 5.70 (d, J_{HH} = 10.0 Hz, 1H), 4.14 (q, J_{HH} = 7.0 Hz, 2H), 2.99−2.87 (m, 1H), 2.44 (dd, J_{HH} = 15.0, 6.5 Hz, 1H), 2.29 (dd, J_{HH} = 15.0, 8.0 Hz, 1H), 1.52−1.40 (m, 1H), 1.36−1.19 (m, 13H), 1.26 (t, J_{HH} = 7.0 Hz, 3H), 0.88 (t, J_{HH} = 6.5 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 171.7, 132.6, 120.9, 60.5, 39.3, 37.2, 34.3, 31.8, 29.5, 29.4, 29.2, 26.9, 22.6, 14.2, 14.1. HRMS (ESI) *m/z*: Calcd for $C_{15}H_{26}O_2{}^{35}Cl_2Na$ $[M + Na]^+$ 331.1202. Found: 331.1203.

*Ethyl 5,5-Dichloro-3-(phenylmethyl)-4-pentenoate (**3e**).* A colorless oil (28 mg, 56% yield). IR (neat) 1734 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ: 7.33−7.15 (m, 5H), 5.78 (d, J_{HH} = 10.0 Hz, 1H), 4.12 (q, J_{HH} = 7.0 Hz, 2H), 3.29−3.16 (m, 1H), 2.73 (d, J_{HH} = 7.0 Hz, 2H), 2.43 (dd, J_{HH} = 15.5, 5.5 Hz, 1H), 2.29 (dd, J_{HH} = 15.5, 8.0 Hz, 1H), 1.25 (t, J_{HH} = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 171.5, 138.2, 131.5, 129.2, 128.4, 126.5, 121.4, 60.6, 39.9, 38.7, 38.0, 14.2. HRMS (ESI) *m/z*: Calcd for $C_{14}H_{17}O_2{}^{35}Cl_2$ $[M + H]^+$ 287.0600. Found: 287.0600.

*Ethyl 3-tert-butyl-5,5-dichloro-4-pentenoate (**3f**).* a colorless oil (35.2 mg, 80%). IR (neat) 1737 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ: 5.74 (d, J_{HH} = 11.0 Hz, 1H), 4.13 (qd, J_{HH} = 7.0, 1.0 Hz, 2H), 2.81 (td, J_{HH} = 11.0, 4.0 Hz, 1H), 2.55 (dd, J_{HH} = 14.0, 4.0 Hz, 1H), 2.15 (dd, J_{HH} = 14.0, 11.0 Hz, 1H), 1.26 (t, J_{HH} = 7.0 Hz, 3H), 0.93 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 172.4, 130.3, 121.5, 60.6, 47.3, 35.3, 34.1, 27.2, 14.2. HRMS (ESI) *m/z*: Calcd for $C_{11}H_{18}O_2{}^{35}Cl_2Na$ $[M + Na]^+$ 275.0576. Found: 275.0574.

*Ethyl 5,5-Dichloro-3-cyclopentyl-4-pentenoate (**3g**).* A colorless oil (40.6 mg, 88% yield). IR (neat) 1737 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ: 5.76 (d, J_{HH} = 10.0 Hz, 1H), 4.13 (q, J_{HH} = 7.0 Hz, 2H), 2.89−2.78 (m, 1H), 2.52 (dd, J_{HH} = 15.0, 5.0 Hz, 1H), 2.26 (dd, J_{HH} = 15.0, 9.0 Hz, 1H) 1.89−1.49 (m, 8H), 1.32−1.14 (m, 1H), 1.26 (t, J_{HH} = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 172.1, 132.0, 121.0, 60.8, 44.3, 42.6, 38.8, 30.8, 30.2, 25.4, 25.3, 14.4. HRMS (ESI) *m/z*: Calcd for $C_{12}H_{19}O_2{}^{35}Cl_2$ $[M + H]^+$ 265.0757. Found: 265.0758.

*N-Methoxy-N-methyl-3-(2,2-dichloroethenyl)heptanamide (**3h**).* A colorless oil (34.3 mg, 74% yield). IR (neat) 1667 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ: 5.74 (d, J_{HH} = 10.0 Hz, 1H), 3.68 (s, 3H), 3.18 (s, 3H), 3.06−2.94 (m, 1H), 2.51 (dd, J_{HH} = 15.0, 7.0 Hz, 1H), 2.44 (dd, J_{HH} = 15.0, 7.0 Hz, 1H), 1.60−1.47 (m, 1H), 1.40−1.21 (m, 5H), 0.89 (t, J_{HH} = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 172.4, 133.2, 120.4, 61.2, 36.8, 36.6, 34.1, 32.1, 29.2, 22.6, 14.0. HRMS (ESI) *m/z*: Calcd for $C_{11}H_{20}NO_2{}^{35}Cl_2$ $[M + H]^+$ 268.0866. Found: 268.0867.

*3-(2,2-Dichloroethenyl)heptanenitrile (**3i**).* A colorless oil (30.2 mg, 84% yield). IR (neat) 2249 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ: 5.76 (d, J_{HH} = 9.5 Hz, 1H), 2.83 (tq, J_{HH} = 9.5, 6.0 Hz, 1H), 2.44 (d, J_{HH} = 6.0 Hz, 2H), 1.67−1.24 (m, 6H), 0.92 (t, J_{HH} = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 130.2, 123.1, 117.5, 36.7, 33.3, 28.9, 22.4, 22.2, 13.9. HRMS (ESI) *m/z*: Calcd for $C_9H_{13}N^{35}Cl_2Na$ $[M + Na]^+$ 228.0317. Found: 228.0317.

*Ethyl 2-Deuterio-3-(2,2-dichloroethenyl)heptanoate (**3a-d**).* A solution of 2,3-*trans*-**1a** (31.6 mg, 0.11 mmol) and AgOAc (21.7 mg, 0.13 mmol) in THF-d_8 (3 mL) was added to a sealed tube. After being stirred at 100 °C for 24 h, the reaction mixture was filtered through a thin pad of Celite. The filtrate was concentrated at reduced pressure. The residue was purified by preparative TLC (hexane:AcOEt = 10:1) to afford **3a′** (4.1 mg, 18%).

A colorless oil (4.1 mg, 18% yield). IR (neat) 1729 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ: 5.70 (d, J_{HH} = 10.0 Hz, 1H), 4.13 (q, J_{HH} = 7.0 Hz, 2H), 2.98−2.88 (m, 1H), 2.38 (d, J_{HH} = 6.0 Hz, 0.5H), 2.28 (d, J_{HH} = 8.0 Hz, 0.5H), 1.51−1.41 (m, 1H), 1.36−1.21 (m, 5H), 1.26 (t, J_{HH} = 7.0 Hz, 3H), 0.89 (t, J_{HH} = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 171.7, 132.5, 120.9, 60.5, 39.0 (t, $^1J_{CD}$ = 20.0 Hz), 37.2, 33.9, 29.1, 22.5, 14.2, 14.0. HRMS (ESI) *m/z*: Calcd for $C_{11}H_{18}{}^2HO_2{}^{35}Cl_2$ $[M + H]^+$ 254.0819. Found: 254.0821.

*3,3-Dichloro-4-methyl-1-(2-propenyl)-2-pyrrolidinone (**7**).*[14c] A solution of trichloroacetamide **6** (42.2 mg, 0.17 mmol) and AgOAc (34.9 mg, 0.21 mmol) in THF (5 mL) was added to a sealed tube. After being stirred at 100 °C for 24 h, the reaction mixture was filtered through a thin pad of Celite. The filtrate was concentrated at reduced pressure. The residue was purified by preparative TLC (hexane:AcOEt = 10:1) to afford **7** (20.0 mg, 55%).

A colorless oil (20.0 mg, 55% yield). IR (neat) 1725 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ: 5.72 (ddt, J_{HH} = 17.0, 10.5, 6.0 Hz, 1H), 5.26 (dq, J_{HH} = 10.5, 1.5 Hz, 1H), 5.24 (dq, J_{HH} = 17.0, 1.5 Hz, 1H), 3.95 (dt, J_{HH} = 6.0, 1.5 Hz, 2H), 3.33 (dd, J_{HH} = 10.0, 7.0 Hz, 1H), 3.03 (dd, J_{HH} = 10.0, 8.5 Hz, 1H), 2.79 (dm, J_{HH} = 8.5 Hz, 1H), 1.34 (d, J_{HH} = 6.5 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 166.8, 130.8, 119.1, 87.1, 49.6, 46.2, 45.4, 11.8. HRMS (ESI) *m/z*: Calcd for $C_8H_{12}NO^{35}Cl_2$ $[M + H^+]$ 208.0291. Found: 208.0287.

*Procedure for Ag(0) Powder-Mediated Ring-Opening Reaction of Cyclopropane **1a**.* A solution of 2,3-*trans*-**1a** (50.0 mg, 0.17 mmol) and Ag(0) powder (45.1 mg, 0.42 mmol) in THF (5 mL) was added to a sealed tube. After being stirred at 100 °C for 24 h, the reaction mixture was filtered through a thin pad of Celite. The filtrate was concentrated at reduced pressure. The residue was purified by preparative TLC (hexane: AcOEt = 10:1) to afford **3a** (29.3 mg, 67%).

*Ethyl 2-[1-Methyl-1-[(tert-butyl)dimethylsiloxy]ethyl]-2-cyclopropene-1-carboxylate (**8**).* To a solution of (1,1-dimethylethyl)[(1,1-dimethyl-2-propynyl)oxy]dimethylsilane (3.6 g, 18 mmol) and $Rh_2(OAc)_4$ (5.3 mg, 0.012 mmol) in CH_2Cl_2 (10 mL) was added a solution of ethyl diazoacetate (684 mg, 6 mmol) by a syringe pump at rate of 1.0 mL/h under argon atmosphere at rt (*Caution! Gas evolution*). After being stirred for overnight, the reaction mixture was filtered through a thin pad of silica gel. The filtrate was concentrated under reduced pressure. The crude product was purified by flash column chromatography (hexane:AcOEt = 10:1) to afford corresponding cyclopropene **8** (740.9 mg, 43%).

A pale yellow oil (740.9 mg, 43% yield). IR (neat): 1728 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ: 6.36 (d, J_{HH} = 1.5 Hz, 1H), 4.20−4.05 (m, 2H), 2.28 (d, J_{HH} = 1.5 Hz, 1H), 1.46 (s, 3H), 1.40 (s, 3H), 1.24 (t, J_{HH} = 7.0 Hz, 3H), 0.87 (s, 9H), 0.09 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 175.7, 120.9, 93.6, 71.2, 60.2, 29.5, 29.2, 25.6, 21.6, 18.0, 14.3, −2.5, −2.6. HRMS (ESI) *m/z*: Calcd for $C_{15}H_{29}O_3Si$ $[M + H]^+$ 285.1881. Found: 285.1879.

*1,2-trans-2,3-trans-3-[1-methyl-1-[(tert-butyl)dimethylsiloxy]-ethyl]-2-trichloromethylcyclopropane-1-carboxylic Acid Ethyl Ester (**9**).* To a solution of ethyl 2-[1-methyl-1-[(*tert*-butyl)dimethylsiloxy]-ethyl]-2-cyclopropene-1-carboxylate (1.0 g, 3.5 mmol) in $CHCl_3$ (35 mL) was added Et_3B (1.0 M in hexane, 7.0 mL, 7.0 mmol) under nitrogen atmosphere at rt. After being stirred at the same temperature for 2 h, the reaction mixture was concentrated at reduced pressure. The crude product was purified by medium-pressure column chromatography (hexane/ethyl acetate = 10/1) to afford cyclopropane **9** (1.17 g, 83%).

White crystals (1.17 g, 83% yield). Mp: 61−65 °C (hexane). IR (neat): 1743 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ: 4.16 (q, J_{HH} = 7.0 Hz, 2H), 3.08 (t, J_{HH} = 6.0 Hz, 1H), 2.24 (dd, J_{HH} = 11.0, 6.0 Hz, 1H), 1.79 (dd, J_{HH} = 11.0, 6.0 Hz, 1H), 1.41 (s, 3H), 1.40 (s, 3H), 1.28 (t, J_{HH} = 7.0 Hz, 3H), 0.88 (s, 9H), 0.14 (s, 3H), 0.03 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 167.9, 99.0, 71.4, 60.9, 40.38, 40.36, 30.9, 29.2, 27.2, 25.9, 14.1, −2.0, −2.3. HRMS (ESI) *m/z*: Calcd for $C_{16}H_{30}O_3{}^{35}Cl_3Si$ $[M + H]^+$ 403.1024. Found: 403.1025.

(1R,5S*,6R*)-4,4-Dimethyl-6-trichloromethyl-3-oxabicyclo-[3.1.0]hexan-2-one (**10**).* To a solution of trichloromethylcyclopropane **9** (1.2 g, 3 mmol) in EtOH (100 mL) was added conc. HCl (30 mL) under nitrogen atmosphere at 40 °C. After being stirred at the same temperature for 17 h, the reaction mixture was poured sat. $NaHCO_3$ and extracted with AcOEt. The organic phase was dried over $MgSO_4$ and concentrated at reduced pressure. The residue was

DOI: 10.1021/acs.joc.6b01508
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purified by flash column chromatography (hexane:AcOEt = 20/1) to afford **10** (560 mg, 77%).

A colorless oil (560 mg, 77% yield). IR (neat): 1772 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ: 2.69 (dd, J_{HH} = 5.5, 3.0 Hz, 1H), 2.56−2.54 (m, 2H), 1.54 (s, 3H), 1.49 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 171.5, 95.5, 82.9, 41.6, 34.3, 28.7, 27.5, 23.6. HRMS (ESI) m/z: Calcd for $C_8H_{10}O_2{}^{35}Cl_3$ $[M + H]^+$ 242.9741. Found: 242.9743.

4-(2,2-Dichloroethenyl)dihydro-5,5-dimethyl-2(3H)-furanone (11). A solution of cyclopropane **10** (97.4 mg, 0.4 mmol) and AgOAc (70.1 mg, 0.42 mmol) in THF (5 mL) was added to a sealed tube. After being stirred at 100 °C for 24 h, the reaction mixture was filtered through a thin pad of Celite. The filtrate was concentrated at reduced pressure. The residue was purified by preparative TLC (hexane: AcOEt = 10:1) to afford **11** (64.7 mg, 77%). The known compound **11** showed satisfactory spectroscopic data in agreement with this reported in the literature.[18b]

A white crystal (64.7 mg, 77% yield). Mp: 115−117 °C (lit.[19b] 116−119 °C). IR (KBr) 1768 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ: 5.81 (d, J_{HH} = 10.0 Hz, 1H), 3.33 (td, J_{HH} = 10.0, 8.5 Hz, 1H), 2.79 (dd, J_{HH} = 17.5, 8.5 Hz, 1H), 2.49 (dd, J_{HH} = 17.5, 10.0 Hz, 1H), 1.50 (s, 3H), 1.33 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 173.8, 126.0, 124.1, 86.2, 46.1, 34.7, 27.8, 23.0. HRMS (ESI) m/z: Calcd for $C_8H_{11}O_2{}^{35}Cl_2$ $[M + H]^+$ 209.0131. Found: 209.0131.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01508.

Copies of ^1H and ^{13}C NMR spectra for all compounds (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: masa-u@kobepharma-u.ac.jp.
*E-mail: miyata@kobepharma-u.ac.jp.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by Grants-in-Aid from the Ministry of Education, Culture, Sports, Science and Technology of Japan (MEXT), the MEXT-Supported Program for the Strategic Research Foundation at Private Universities, and the Uehara Memorial Foundation.

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DOI: 10.1021/acs.joc.6b01508
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