Electronic Supplementary Material (ESI) for ChemComm.

Reaction of cyclopropenes with a trichloromethyl radical: unprecedented ring-opening reaction of cyclopropanes with migration

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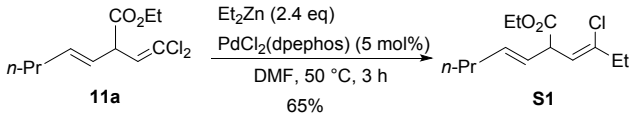
Pd-catalyzed *trans*-selective monoalkylation of dichloroalkene

To demonstrate the synthetic utility of the dichloroalkene, we investigated the *trans*-selective monoalkylation reaction. The palladium-catalyzed coupling reaction of **11a** with diethylzinc afforded the (*Z*)-trisubstituted alkene in good yield.



Experimental section

General

NMR spectra were recorded at 300 MHz/75 MHz (^{1}H NMR/^{13}C NMR) or 500 MHz/125 MHz (^{1}H NMR/^{13}C NMR) using Varian Gemini-300 (300 MHz), Varian MERCURY plus 300 (300 MHz), or Varian NMR system AS 500 (500 MHz) spectrometers. Chemical shifts (δ) are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, br = broad), coupling constants, and integration. IR spectra were obtained on a Perkin Elmer SpectrumOne A spectrometer. Mass spectra were obtained by EI, CI, ESI or APCI methods on a Hitachi M-4100 and Thermo Fisher Scientific Exactive. Preparative TLC separations 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.

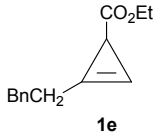
General Procedure for Preparation of Cyclopropenes.

To a solution of alkyne (25 mmol) and $Rh_2(OAc)_4$ (0.04 mmol) in CH_2Cl_2 (10 mL) was added a solution of ethyl diazoacetate (17.5 mmol) in CH_2Cl_2 (2.5 mL) by a syringe pump at rate of 1.0 mL/h under argon atmosphere at rt. 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 cyclopropenes.

The physical and spectroscopic data of **1a** [1], **1b** [1], **1c** [1], **1d** [1] and **1f** [2] are in consistent with those reported in the literature.

Ethyl 2-(2-Phenylethyl)-2-cyclopropene-1-carboxylate (1e)

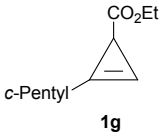


1e

According to general procedure, cyclopropene **1e** was prepared from 4-phenyl-1-butyne.

A colorless oil. IR (neat) : 1722 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ : 7.32-7.20 (5H, m), 6.35 (1H, q, *J*=1.5Hz), 4.18-4.07 (2H, m), 2.95-2.79 (4H, m), 2.14 (1H, d, *J*=1.5 Hz), 1.25 (3H, t, *J*=7.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ : 176.4, 140.7, 128.4, 128.3, 126.2, 114.9, 94.9, 60.2, 32.9, 26.7, 19.8, 14.4. HRMS (ESI) *m/z* : Calcd for $C_{14}H_{16}O_2Na$ $[M+Na]^+$ 239.1043. Found : 239.1044.

Ethyl 2-Cyclopentyl-2-cyclopropene-1-carboxylate (1g)

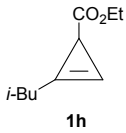


1g

According to general procedure, cyclopropene **1g** was prepared from cyclopentylacetylene.

A colorless oil. IR (neat) : 1724 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ : 6.26 (1H, t, *J*=1.0 Hz), 4.19-4.07 (2H, m), 3.06-2.98 (1H, m), 2.15 (1H, d, *J*=1.0 Hz), 1.93-1.83 (2H, m), 1.70-1.57 (6H, m), 1.25 (3H, t, *J*=7.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ : 175.9, 118.4, 91.9, 59.4, 34.9, 30.4, 30.0, 24.6, 19.2, 13.7. HRMS (ESI) *m/z* : Calcd for $C_{11}H_{16}O_2Na$ $[M+Na]^+$ 203.1043. Found : 203.1045.

Ethyl 2-(2-methylpropyl)-2-cyclopropene-1-carboxylate (1h)

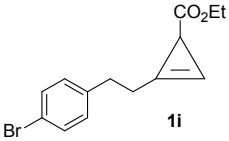


1h

According to general procedure, cyclopropene **1h** was prepared from 4-methyl-1-pentyne.

A colorless oil. IR (neat) : 1712 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ : 6.38-6.34 (1H, m), 4.15-4.09 (2H, m), 2.41-2.36 (2H, m), 2.13-2.11 (1H, m), 1.99-1.90 (1H, m), 1.25 (3H, t, *J*=7.5 Hz), 0.98 (6H, t, *J*=7.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ : 176.7, 114.7, 94.5, 60.1, 33.9, 26.8, 22.3, 19.7, 14.4. HRMS (ESI) *m/z* : Calcd for $C_{10}H_{17}O_2$ $[M+H]^+$ 169.1223. Found : 169.1218.

Ethyl 2-[2-(4-Bromophenyl)ethyl]-2-cyclopropene-1-carboxylate (1i)

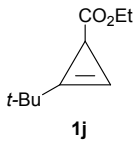


1i

According to general procedure, cyclopropene **1i** was prepared from 1-bromo-4-(3-butynyl)benzene.

A colorless oil. IR (neat) : 1720 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ : 7.41 (2H, br d, *J*=8.0 Hz), 7.09 (2H, br d, *J*=8.0 Hz), 6.36 (1H, q, *J*=1.5Hz), 4.17-4.06 (2H, m), 2.90-2.76 (4H, m), 2.12 (1H, d, *J*=1.5 Hz), 1.25 (3H, t, *J*=7.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ : 176.3, 139.5, 131.5, 130.1, 120.0, 114.5, 95.2, 60.2, 32.2, 26.4, 19.8, 14.3. HRMS (ESI) *m/z* : Calcd for $C_{14}H_{15}O_2{}^{79}BrNa$ $[M+Na]^+$ 317.0148. Found : 317.0151

Ethyl 2-(1,1-Dimethylethyl)-2-cyclopropene-1-carboxylate (1j)



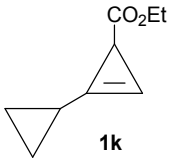
1j

According to general procedure, cyclopropene **1j** was prepared from 3,3-dimethyl-1-buthyne.

A colorless oil. IR (neat) : 1726 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ : 6.21 (1H, d, *J*=1.5 Hz), 4.30-4.06 (2H, m), 2.17 (1H, d, *J*=1.5 Hz), 1.24 (3H, t, *J*=7.0 Hz), 1.18 (9H, s). ^{13}C NMR (75 MHz,

$CDCl_3$) δ : 176.6, 123.3, 91.9, 60.0, 31.2, 27.7, 19.8, 14.3. HRMS (ESI) *m/z* : Calcd for $C_{10}H_{16}O_2Na$ $[M+Na]^+$ 191.1043. Found : 191.1044.

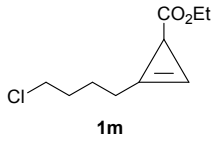
Ethyl 2-Cyclopropyl-2-cyclopropene-1-carboxylate (1k)



1k

According to general procedure, cyclopropene **1k** was prepared from cyclopropylacetylene. A colorless oil. IR (neat) : 1725 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ : 6.24 (1H, d, *J*=2.0 Hz), 4.20-4.04 (2H, m), 2.05 (1H, d, *J*=2.0 Hz), 1.86 (1H, tt, *J*=8.0, 5.0 Hz), 1.25 (3H, t, *J*=7.0 Hz), 1.00-0.80 (3H, m), 0.66-0.60 (1H, m). ^{13}C NMR (75 MHz, $CDCl_3$) δ : 176.2, 117.4, 91.7, 60.1, 18.6, 14.3, 6.8, 5.9, 5.8. HRMS (ESI) *m/z* : Calcd for $C_9H_{12}O_2$ $[M+H]^+$ 153.0910. Found : 153.0909.

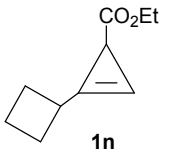
Ethyl 2-(4-chlorobutyl)-2-cyclopropene-1-carboxylate (1m)



1m

According to general procedure, cyclopropene **1m** was prepared from 6-chloro-1-hexyne. A colorless oil. IR (neat) : 1711 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ : 6.39 (1H, t, *J*=1.5 Hz), 4.18-4.08 (2H, m), 3.56 (2H, t, *J*=6.5 Hz), 2.55 (2H, t, *J*=7.0 Hz), 2.15 (1H, t, *J*=1.5 Hz), 1.92-1.70 (4H, m), 1.26 (3H, t, *J*=7.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ : 176.0, 114.6, 94.5, 59.9, 44.2, 31.5, 24.0, 23.7, 19.4, 14.1. HRMS (ESI) *m/z* : Calcd for $C_{10}H_{16}O_2Cl$ $[M+H]^+$ 203.0833. Found : 203.0831.

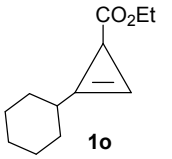
Ethyl 2-Cyclobutyl-2-cyclopropene-1-carboxylate (1n)



1n

According to general procedure, cyclopropene **1n** was prepared from cyclobutylacetylene. A colorless oil. IR (neat) : 1714 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ : 6.30 (1H, t, *J*=1.0 Hz), 4.23-4.06 (2H, m), 3.48-3.36 (1H, m), 2.34-2.20 (2H, m), 2.20 (1H, t, *J*=1.5 Hz), 2.18-1.89 (4H, m), 1.26 (3H, t, *J*=7.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ :176.5, 117.9, 92.4, 60.0, 30.3, 27.0, 26.6, 19.5, 19.0, 14.2. HRMS (ESI) *m/z* : Calcd for $C_{10}H_{15}O_2$ $[M+H]^+$ 167.1067. Found : 167.1066.

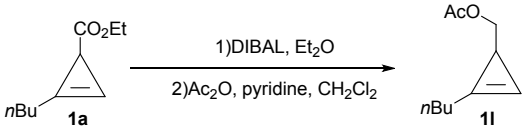
Ethyl 2-Cyclohexyl-2-cyclopropene-1-carboxylate (1o)



1o

According to general procedure, cyclopropene **1o** was prepared from cyclohexylacetylene. A colorless oil. IR (neat) : 1724 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ : 6.29 (1H, d, *J*=1.5 Hz), 4.20-4.05 (2H, m), 2.62-2.51 (1H, m), 2.13 (1H, d, *J*=2.0 Hz), 1.94-1.79 (2H, m), 1.76-1.54 (4H, m),1.43-1.24 (4H, m), 1.25 (3H, t, *J*=7.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ :176.6, 119.0, 92.6, 59.9, 34.1, 30.09, 30.06, 25.8, 25.04, 24.99. 19.1, 14.2. HRMS (ESI) *m/z* : Calcd for $C_{12}H_{19}O_2$ $[M+H]^+$ 195.1380. Found : 195.1384.

2-Butyl-2-cyclopropene-1-methanol 1-Acetate (1l)



To a solution of ester **1a** (1.5 g, 8.9 mmol) in Et_2O (1.5 ml) was added dropwise DIBAL-H (1.0 M in toluene, 17.8

mL, 17.8 mmol) under nitrogen atmosphere at -78 °C. After being stirred at the same temperature for 1 h and then stirred at rt for 1 h, the reaction mixture was diluted with sat. NH_4Cl, acidified with sat. HCl and extracted with Et_2O. The organic phase was washed with sat. $NaHCO_3$ and sat. NaCl, dried over $MgSO_4$ and concentrated at reduced pressure. The residue was purified by flash column chromatography (hexane : AcOEt = 5 : 1) to afford 2-butyl-2-cyclopropene-1-methanol as a colorless oil. To a solution of the alcohol (650 mg, 5.1 mmol) and pyridine (1.0 mL) in CH_2Cl_2 (6.6 mL) was added acetic anhydride (0.74 mL) under nitrogen atmosphere at at rt. After being stirred for 2 h at the same temperature, the reaction mixture was diluted with H_2O and extracted with CH_2Cl_2. The organic phase was dried over $MgSO_4$ and concentrated at reduced pressure. The residue was purified by flash column chromatography (hexane : Et_2O = 5 : 1) to afford **1l** as a colorless oil.

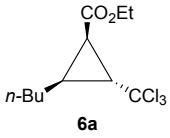
IR (neat) : 1739 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ : 6.57 (1H, br s), 3.94 (2H, d, *J*=5.0 Hz), 2.47 (2H, t, *J*=7.0 Hz), 2.06 (3H, s), 1.68 (1H, td, *J*=5.0, 1.5 Hz), 1.60-1.50 (2H, m), 1.43-1.34 (2H, m), 0.92 (3H, t, J=7.5 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ : 171.3, 124.8, 101.6, 72.2, 29.1, 25.7, 22.3, 21.1, 16.6, 13.8. HRMS (ESI) *m/z* : Calcd for $C_{10}H_{16}O_2Na$ $[M+Na]^+$ 191.1043. Found : 191.1045.

General Procedure for Triethylborane-mediated Trichloromethyl Radical Addition to Cyclopropenes.

To a solution of cyclopropene (1.0 mmol) in $CHCl_3$ (10 mL) was added Et_3B (1.0 M in hexane, 0.5-2.0 mL, 0.5-2.0 mmol) under nitrogen atmosphere at rt. After being stirred at the same temperature for 2 h, the reaction mixture was diluted with H_2O and extracted with $CHCl_3$. The organic phase was dried over $MgSO_4$ and concentrated at reduced pressure. The crude product was purified by medium-pressure column chromatography (hexane) to afford the corresponding cyclopropanes.

Ethyl 3-Butyl-2-(trichloromethyl)cyclopropane-1-carboxylate (6a, 7a)

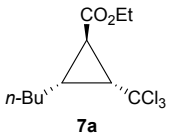
1,2-*trans*-2,3-*trans*-6a



6a

A colorless oil. IR (neat) : 1732 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ : 4.21-4.16 (2H, m), 2.71 (1H, dd, *J*=6.5, 5.0 Hz), 2.29 (1H, dd, *J*=10.0, 5.0 Hz), 1.86 (1H, ddt, J=10.0, 7.0, 6.5 Hz), 1.67-1.54 (2H, m), 1.44-1.32 (4H, m), 1.29 (3H, t, *J*=7.0 Hz), 0.96 (3H, t, *J*=7.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ : 169.7, 98.3, 61.1, 45.7, 31.2, 29.5, 27.1, 25.3, 22.2, 14.2, 14.0. HRMS (CI) *m/z* : Calcd for $C_{11}H_{18}Cl_3O_2$ $[M+H]^+$ 287.0372. Found : 287.0362.

1,2-*trans*-2,3-*cis*-7a

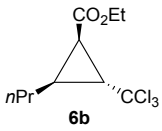


7a

A colorless oil. IR (neat) : 1732 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ : 4.18 (2H, q, *J*=7.0 Hz), 2.84 (1H, dd, *J*=9.5, 5.0 Hz), 2.25 (1H, t, *J*=5.0 Hz), 1.96-1.89 (1H, m), 1.81-1.69 (2H, m), 1.49-1.44 (2H, m),1.38-1.33 (2H, m) 1.30 (3H, t, *J*=7.0 Hz), 0.91 (3H, t, *J*=7.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ : 171.8, 97.3, 61.2, 45.8, 31.9, 31.1, 28.6, 24.5, 22.3, 14.2, 13.9. HRMS (CI) *m/z* : Calcd for $C_{11}H_{18}Cl_3O_2$ $[M+H]^+$ 287.0371. Found : 287.0364.

Ethyl 2-Trichloromethyl-3-propylcyclopropane-1-carboxylate (6b, 7b)

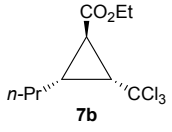
1,2-*trans*-2,3-*trans*-6b



6b

A colorless oil. IR (neat) : 1732 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ : 4.18 (2H, q, *J*=7.0 Hz), 2.71 (1H, dd, *J*=6.0, 5.0 Hz), 2.29 (1H, dd, *J*=10.0, 5.0 Hz), 1.86 (1H, ddt, J=10.0, 7.0, 6.0 Hz), 1.70-1.25 (4H, m), 1.29 (3H, t, *J*=7.0 Hz), 0.94 (3H, t, *J*=7.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ : 169.7, 98.3, 61.0, 45.6, 29.3, 27.6, 27.1, 22.2, 14.2, 13.7. HRMS (CI) *m/z* : Calcd for $C_{10}H_{16}Cl_3O_2$ $[M+H]^+$ 273.0215. Found : 273.0208.

1,2-*trans*-2,3-*cis*-7b

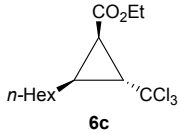


7b

A colorless oil. IR (neat) : 1722 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ : 4.18 (2H, q, *J*=7.0 Hz), 2.84 (1H, dd, *J*=9.0, 5.0 Hz), 2.25 (1H, t, *J*=5.0 Hz), 1.93-1.88 (1H, m), 1.78-1.70 (2H, m), 1.58-1.42 (2H, m),1.29 (3H, t, *J*=7.0 Hz), 0.95 (3H, t, *J*=7.5 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ : 171.8, 97.3, 61.2, 45.6, 30.9, 28.6, 26.8, 22.9, 14.2, 13.7. HRMS (CI) *m/z* : Calcd for $C_{10}H_{16}Cl_3O_2$ $[M+H]^+$ 273.0215. Found : 273.0200.

Ethyl 2-Trichloromethyl-3-hexylcyclopropane-1-carboxylate (6c, 7c)

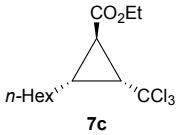
1,2-*trans*-2,3-*trans*-6c



6c

A colorless oil. IR (neat) : 1732 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ : 4.18 (2H, q, *J*=7.0 Hz), 2.71 (1H, dd, *J*=6.0, 5.0 Hz), 2.28 (1H, dd, *J*=10.0, 5.0 Hz), 1.86 (1H, ddt, J=10.0, 7.5, 6.0 Hz), 1.68-1.49 (2H, m), 1.45-1.20 (8H, m), 1.29 (3H, t, *J*=7.0 Hz), 0.88 (3H, t, *J*=7.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ : 169.6, 98.3, 61.0, 45.7, 31.7, 29.5, 29.0, 28.8, 27.1, 25.6, 22.5, 14.2, 14.0. HRMS (CI) *m/z* : Calcd for $C_{13}H_{22}Cl_3O_2$ $[M+H]^+$ 315.0684. Found : 315.0662.

1,2-*trans*-2,3-*cis*-7c

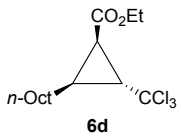


7c

A colorless oil. IR (neat) : 1722 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ : 4.18 (2H, q, *J*=7.0 Hz), 2.84 (1H, dd, *J*=9.5, 5.0 Hz), 2.25 (1H, t, *J*=5.0 Hz), 1.98-1.85 (1H, m), 1.80-1.66 (2H, m), 1.51-1.40 (2H, m), 1.40-1.23 (6H, m) 1.29 (3H, t, *J*=7.0 Hz), 0.88 (3H, t, *J*=7.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ : 171.8, 97.3, 61.2, 45.7, 31.6, 31.1, 29.7, 28.8, 28.6, 24.8, 22.6, 14.2, 14.0. HRMS (CI) *m/z* : Calcd for $C_{13}H_{22}Cl_3O_2$ $[M+H]^+$ 315.0684. Found : 315.0663.

Ethyl 2-Trichloromethyl-3-octylcyclopropane-1-carboxylate (6d,7 d)

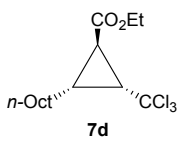
1,2-*trans*-2,3-*trans*-6d



6d

A colorless oil. IR (neat) : 1724 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ : 4.18 (2H, q, *J*=7.0 Hz), 2.71 (1H, dd, *J*=5.0, 1.0 Hz), 2.29 (1H, ddd, *J*=10.0, 5.0, 1.0 Hz), 1.91-1.81 (1H, m), 1.68-1.49 (2H, m), 1.47-1.20 (14H, m), 1.29 (3H, t, *J*=7.0 Hz), 0.88 (3H, t, *J*=6.5 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ : 169.7, 98.3, 61.0, 45.7, 31.8, 29.50, 29.45, 29.2, 29.1, 29.0, 27.1, 25.6, 22.6, 14.2, 14.1. HRMS (APCI) *m/z* : Calcd for $C_{15}H_{26}Cl_3O_2$ $[M+H]^+$ 343.0993. Found : 343.0992.

1,2-*trans*-2,3-*cis*-7d



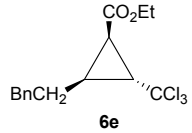
7d

A colorless oil. IR (neat) : 1722 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ : 4.18 (2H, q, *J*=7.0 Hz),

2.84 (1H, dd, *J*=9.5, 5.0 Hz), 2.25 (1H, t, *J*=5.0 Hz), 1.95-1.88 (1H, m), 1.80-1.69 (2H, m), 1.52-1.44 (2H, m), 1.34-1.26 (10H, m), 1.29 (3H, t, *J*=7.0 Hz), 0.88 (3H, t, *J*=6.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ : 171.8, 97.3, 61.2, 45.7, 31.8, 31.2, 29.8, 29.4, 29.24, 29.18, 28.6, 24.8, 22.7, 14.2, 14.1. HRMS (APCI) *m/z* : Calcd for $C_{15}H_{26}Cl_3O_2$ $[M+H]^+$ 343.0993. Found : 343.0992.

Ethyl 2-Trichloromethyl-3-(2-phenylethyl)cyclopropane-1-carboxylate (6e, 7e)

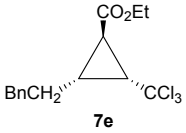
1,2-*trans*-2,3-*trans*-6e



6e

A colorless oil. IR (neat) : 1728 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ : 7.30-7.26 (2H, m), 7.21-7.18 (3H, m), 4.18-4.14 (2H, m), 2.77 (1H, dd, *J*=5.0, 4.5 Hz), 2.76-2.72 (1H, m), 2.68-2.62 (1H, m), 2.30 (1H, dd, *J*=9.5, 5.0 Hz), 2.03-1.98 (1H, m), 1.93-1.87 (2H, m), 1.28 (3H, t, *J*=7.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ : 169.6, 141.0, 128.5, 128.4, 98.1, 61.2, 45.8, 35.2, 28.9, 27.6, 27.0, 14.2. HRMS (EI) *m/z* : Calcd for $C_{15}H_{17}Cl_3O_2$ $[M^+]$ 334.0293. Found : 334.0298.

1,2-*trans*-2,3-*cis*-7e

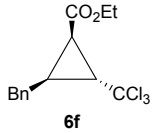


7e

A colorless oil. IR (neat) : 1729 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ :7.30-7.25(2H, m), 7.21-7.17 (3H, m), 4.18-4.12 (2H, m), 2.88-2.82 (1H, m), 2.84 (1H, dd, *J*=9.5, 5.0 Hz), 2.79-2.73 (1H, m), 2.30-2.22 (1H, m), 2.20 (1H, dd, *J*=6.0, 5.0 Hz), 2.16-2.00 (1H, m), 1.75 (1H, tt, *J*=9.5, 6.0 Hz), 1.28 (3H, t, *J*=7.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ : 171.6, 141.0, 128.5, 128.4, 126.1, 97.1, 61.2, 45.6, 35.8, 30.4, 28.5, 26.7, 14.2. HRMS (EI) *m/z* : Calcd for $C_{15}H_{17}Cl_3O_2$ $[M^+]$ 343.0293. Found : 334.0309.

Ethyl 2-Trichloromethyl-3-(phenylmethyl)cyclopropane-1-carboxylate (6f, 7f)

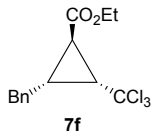
1,2-*trans*-2,3-*trans*-6f



6f

A colorless oil. IR (neat) : 1721 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ : 7.31-7.27 (2H, m), 7.22-7.20 (3H, m), 4.20-4.16 (2H, m), 3.05 (1H, dd, *J*=15.5, 6.5 Hz), 2.89-2.94 (2H, m), 2.37 (1H, dd, J=10.0, 5.0 Hz), 2.16 (1H, ddt, *J*=10.0, 8.0, 6.5 Hz), 1.25 (3H, t, *J*=7.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ : 169.7, 139.5, 128.5, 128.4, 126.4, 97.9, 61.2, 45.7, 31.6, 30.1, 27.0, 14.2. HRMS (EI) *m/z* : Calcd for $C_{14}H_{15}Cl_3O_2$ $[M^+]$ 320.0137. Found : 320.0129.

1,2-*trans*-2,3-*cis*-7f

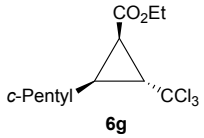


7f

A colorless oil. IR (neat) : 1723 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ :7.32-7.29 (2H, m), 7.26-7.21 (3H, m), 4.19-4.14 (2H, m), 3.25 (1H, dd, *J*=15.0, 5.0 Hz), 3.15 (1H, dd, *J*=15.0, 9.5 Hz), 2.95 (1H, dd, *J*=9.5, 5.0 Hz), 2.47 (1H, t, *J*=5.0 Hz), 2.10-2.00 (1H, m), 1.27 (3H, t, *J*=7.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ : 171.3, 139.9, 128.6, 128.4, 126.4, 96.9, 61.3, 45.6, 31.2, 30.6, 28.8, 14.1. HRMS (EI) *m/z* : Calcd for $C_{14}H_{15}Cl_3O_2$ $[M^+]$ 320.0137. Found : 320.0133.

Ethyl 2-Trichloromethyl-3-cyclopentylcyclopropane-1-carboxylate (6g, 7g)

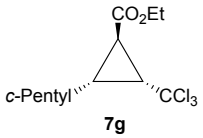
1,2-*trans*-2,3-*trans*-6g



6g

A colorless oil. IR (neat) 1731 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ : 4.24-4.13 (2H, m), 2.78 (1H, dd, *J*=6.0, 5.0 Hz), 2.31 (1H, dd, *J*=10.0, 5.0 Hz), 2.00-1.84 (2H, m), 1.75-1.42 (8H, m), 1.29 (3H, t, *J*=7.0 Hz), 0.96 (3H, t, *J*=7.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ : 169.8, 98.2, 61.0, 45.8, 36.9, 34.7, 32.4, 31.9, 27.3, 25.1, 25.0, 14.2. HRMS (CI) *m/z* : Calcd for $C_{12}H_{18}Cl_3O_2$ $[M+H]^+$ 299.0371. Found : 299.0364.

1,2-*trans*-2,3-*cis*-7g

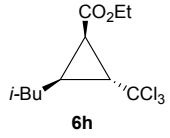


7g

A colorless oil. IR (neat) 1731 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ : 4.18 (2H, q, *J*=7.0 Hz), 2.86 (1H, dd, *J*=9.5, 5.0 Hz), 2.36 (1H, dt, *J*=11.0, 8.0 Hz), 2.26 (1H, dd, J=6.0, 5.0 Hz), 2.03-1.84 (2H, m), 1.74-1.27 (7H, m), 1.29 (3H, t, *J*=7.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ : 171.9, 97.3, 61.2, 46.5, 37.3, 35.8, 33.9, 32.9, 28.1, 25.6, 25.0, 14.2. HRMS (CI) *m/z* : Calcd for $C_{12}H_{18}Cl_3O_2$ $[M+H]^+$ 299.0372. Found : 299.0360.

Ethyl 2-Trichloromethyl-3-(2-methylpropyl)cyclopropane-1-carboxylate (6h, 7h)

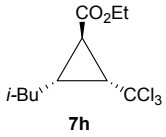
1,2-*trans*-2,3-*trans*-6h



6h

A colorless oil. IR (neat) 1722 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ : 4.18 (2H, q, *J*=7.0 Hz), 2.71 (1H, t, *J*=6.0 Hz), 2.29 (1H, dd, *J*=10.0, 5.0 Hz), 1.91 (1H, dq, *J*=10.0, 7.0 Hz), 1.70-1.53 (2H, m), 1.48-1.39 (1H, m), 1.29 (3H, t, *J*=7.0 Hz), 0.96 (3H, d, *J*=6.5 Hz), 0.92 (3H, d, *J*=6.5 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ : 169.7, 98.4, 61.0, 45.5, 34.4, 28.2, 27.1, 22.6, 22.0, 14.2. HRMS (ESI) *m/z* : Calcd for $C_{11}H_{17}Cl_3O_2Na$ $[M+Na]^+$ 309.0186. Found : 309.0183.

1,2-*trans*-2,3-*cis*-7h

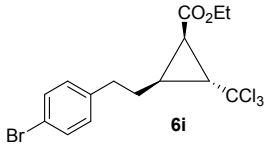


7h

A colorless oil. IR (neat) 1721 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ : 4.19 (2H, q, *J*=7.0 Hz), 2.83 (1H, dd, *J*=9.5, 5.0 Hz), 2.26 (1H, t, *J*=5.0 Hz), 1.91-1.84 (1H, m), 1.81-1.68 (2H, m), 1.54-1.64 (1H, m), 1.30 (3H, t, *J*=7.0 Hz), 0.96 (3H, d, *J*=6.5 Hz), 0.95 (3H, d, *J*=6.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ : 171.8, 97.3, 61.2, 45.2, 33.6, 29.7, 29.0, 28.8, 22.6, 21.9, 14.2. HRMS (ESI) *m/z* : Calcd for $C_{11}H_{17}Cl_3O_2Na$ $[M+Na]^+$ 309.0186. Found : 309.0179.

Ethyl 2-Trichloromethyl-3-[2-(4-Bromophenyl)ethyl]cyclopropane-1-carboxylate (6i, 7i)

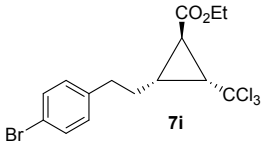
1,2-*trans*-2,3-*trans*-6i



6i

A colorless oil. IR (neat) 1728 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ : 7.40 (2H, br d, *J*=8.5 Hz), 7.06 (2H, br d, *J*=8.0 Hz), 4.20-4.09 (2H, m), 2.75 (1H, dd, *J*=5.5, 5.0 Hz), 2.74-2.68 (1H, m), 2.64-2.58 (1H, m), 2.28 (1H, dd, J=10.0, 5.5 Hz), 2.01-1.96 (1H, m), 1.91-1.84 (1H, m), 1.80-1.74 (1H, m), 1.28 (3H, t, *J*=7.5 Hz,). ^{13}C NMR (125 MHz, $CDCl_3$) δ : 169.6, 139.9, 131.5, 130.2 119.8, 98.0, 61.2, 45.8, 34.6, 28.7, 27.3, 27.0, 14.2. HRMS (EI) *m/z* : Calcd for $C_{15}H_{16}{}^{79}BrCl_3O_2$ $[M^+]$ 411.9398. Found : 411.9410.

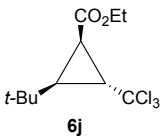
1,2-*trans*-2,3-*cis*-7i



7i

A colorless oil. IR (neat) 1729 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ :7.40 (2H, br d, *J*=8.5 Hz), 7.04 (2H, br d, *J*=8.5 Hz), 4.18-4.09 (2H, m), 2.83 (1H, dd, *J*=9.5, 5.0 Hz), 2.83-2.79 (1H, m), 2.73-2.67 (1H, m), 2.25 (1H, ddt, *J*=14.5, 8.5, 5.0 Hz), 2.16 (1H, t, *J*=5.0 Hz), 2.13-2.05 (1H, m), 1.70 (1H, tt, *J*=9.5. 5.0 Hz), 1.29 (3H, t, *J*=7.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ : 171.4, 139.9, 131.5, 130.2, 119.1, 97.0, 61.3, 45.4, 35.2, 30.1, 28.5, 26.5, 14.2. HRMS (EI) *m/z* : Calcd for $C_{15}H_{16}{}^{79}BrCl_3O_2$ $[M^+]$ 411.9399. Found : 411.9402.

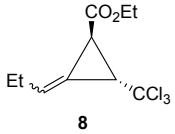
1,2-*trans*-2,3-*trans*-Ethyl 2-Trichloromethyl-3-(1,1-dimethylethyl)cyclopropane-1-carboxylate (6j)



6j

A colorless oil. IR (neat) 1732 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ : 4.24-4.12 (2H, m), 3.00 (1H, dd, *J*=7.0, 5.5 Hz), 2.22 (1H, dd, *J*=11.0, 5.5 Hz), 1.73 (1H, dd, J=11.0, 7.0 Hz), 1.29 (3H, t, *J*=7.0 Hz), 1.02 (9H, s). ^{13}C NMR (125 MHz, $CDCl_3$) δ : 169.5, 99.0, 61.1, 42.0, 40.4, 30.6, 29.4, 27.7, 14.1. HRMS (EI) *m/z* : Calcd for $C_{11}H_{18}Cl_3O_2$ $[M+H]^+$ 287.0371. Found : 287.0370.

Ethyl (*E/Z*)-2-Trichloromethyl-3-propylidenecyclopropane-1-carboxylate (8)

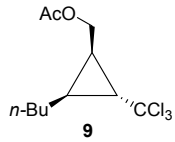


8

A colorless oil. 1:1 mixture of *E*/*Z* isomers. IR (neat) 1732 cm^{-1}. ^1H-NMR (300 MHz, $CDCl_3$) δ : 6.27 (1/2H, tt, *J*=6.0, 2.0 Hz), 6.10 (1/2H, tt, *J*=7.5 2.0 Hz), 4.24-4.15 (2/2H, m), 4.19 (2/2H, q, *J*=7.0 Hz), 3.45-3.42 (1/2H, m), 3.38-3.35 (1/2H, m), 2.77-2.74 (1/2H, m), 2.70-2.68 (1/2H, m), 2.40-2.20 (4/2H, m) 1.29 (3H, t, *J*=7.0 Hz), 1.08 (3/2H, t, *J*=7.0 Hz), 1.07 (3/2H, t, *J*=7.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ : 169.5, 169.4, 127.5, 125.9, 120.1, 119.9, 96.8, 96.6, 61.4, 61.3, 42.3, 41.1, 26.2, 26.1, 25.3, 24.6, 14.12, 14.09, 13.5, 12.6. HRMS (EI) *m/z* : Calcd for $C_{10}H_{13}Cl_3O_2$ $[M+H]^+$ 269.9980. Found : 269.9954.

3-Butyl-2-(trichloromethyl)cyclopropane-1-methanol 1-Acetate (9)

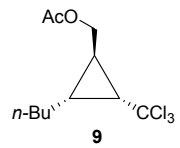
1,2-*trans*-2,3-*trans*-9



9

A colorless oil. IR (neat) 1743 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ : 4.23 (1H, dd, *J*=11.5, 7.5 Hz), 4.11 (1H, dd, *J*=11.5, 7.5 Hz), 2.07 (3H, s), 1.95 (1H, t, *J*=5.0 Hz), 1.82 (1H, ddt, *J*=9.5, 7.5, 5.0 Hz), 1.60-1.52 (1H, m), 1.52-1.33 (6H, m), 0.91 (3H, t, *J*=7.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ : 171.0, 99.7, 62.0, 44.9, 31.6, 26.8, 25.9, 24.1, 22.4, 21.0, 14.0. HRMS (ESI) *m/z* : Calcd for $C_{11}H_{17}Cl_3O_2Na$ $[M+Na]^+$ 309.0186. Found : 309.0191.

1,2-*trans*-2,3-*cis*-9



9

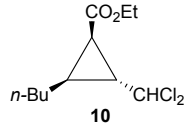
A colorless oil. IR (neat) 1743 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ : 4.10 (1H, dd, *J*=11.5, 7.5 Hz), 4.03 (1H, dd, *J*=11.5, 7.5 Hz), 2.22 (1H, dd, *J*=9.5, 5.5 Hz), 2.07 (3H, s), 1.89-1.80 (2H, m), 1.74-1.66 (1H, m), 1.47-1.28 (4H, m), 1.22-1.16 (1H, m) , 0.91 (3H, t, *J*=7.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ : 171.0, 98.9, 66.0, 43.5, 32.2, 28.0, 26.5, 24.7, 22.3, 20.9, 14.0. HRMS (ESI) *m/z* : Calcd for $C_{11}H_{17}Cl_3O_2Na$ $[M+Na]^+$ 309.0186. Found : 309.0191.

Ethyl 3-Butyl-2-(dichloromethyl)cyclopropane-1-carboxylate (10)

To a solution of cyclopropene **1a** (168 mg, 1.0 mmol) in CH_2Cl_2 (10 mL) was added Et_3B (1.0 M in hexane, 1.0

mL, 1.0 mmol) under nitrogen atomosphere at rt. After being stirred at the same temperature for 6 h, the reaction mixture was diluted with H_2O and extracted with $CHCl_3$. The organic phase was dried over $MgSO_4$ and concentrated at reduced pressure. The residue was purified by medium-pressure column chromatography (hexane) to afford **10** (157mg, 62%, dr = 76:14) as a colorless oil.

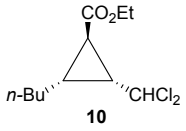
1,2-*trans*-2,3-*trans* isomer (10)



10

A colorless oil. IR (neat) 1728 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ : 5.51 (1H, d, J=7.0 Hz), 4.18-4.14 (2H, m), 2.23-2.19 (1H, m), 1.98 (1H, dd, *J*=9.0, 5.0 Hz), 1.63-1.51 (3H, m), 1.47-1.26 (4H, m), 1.28 (3H, t, *J*=7.0 Hz), 0.89 (3H, t, *J*=7.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ : 170.2, 73.4, 60.8, 36.6, 31.3, 28.7, 26.1, 25.6, 22.2, 14.2, 14.0. HRMS (CI) *m/z* : Calcd for $C_{11}H_{19}Cl_2O_2$ $[M+H]^+$ 253.0761 Found : 253.0753.

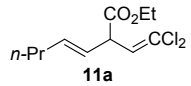
1,2-*trans*-2,3-*cis* isomer (10)



10

A colorless oil. IR (neat) 1723 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ : 5.37 (1H, d, *J*=10.0 Hz,), 4.15 (2H, q, *J*=7.0 Hz), 2.42 (1H, ddd, *J*=10.0, 9.0, 5.0 Hz), 1.76-1.70 (1H, m), 1.68-1.61 (1H, m), 1.55 (1H, t, *J*=5.0 Hz), 1.48-1.24 (5H, m), 1.27 (3H, t, *J*=7.0 Hz), 0.91 (3H, t, *J*=7.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ : 171.8, 71.1, 61.0, 37.6, 31.4, 30.0, 28.9, 26.7, 22.3, 14.2, 13.9. HRMS (CI) *m/z* : Calcd for $C_{11}H_{19}Cl_2O_2$ $[M+H]^+$ 253.0761. Found : 253.0763.

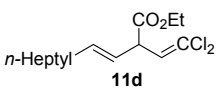
Ethyl (*E*)-2-(2,2-Dichloroethenyl)-3-heptenoate (11a)



11a

Me_2Zn (1.0 M in hexane, 0.3 mL, 0.3 mmol) was added four times at 1 h intervals to a solution of **1a** (50.5 mg, 0.3 mmol) in $CHCl_3$ (2.5 mL) under nitrogen atomosphere at rt. After being stirred at the same temperature for 24 h, the reaction mixture was diluted with sat. NH_4Cl and extracted with $CHCl_3$. The organic phase was dried over $MgSO_4$ and concentrated at reduced pressure. The residue was purified by preparative TLC (hexane : AcOEt = 20 : 1) to afford **11a** (55.2 mg, 74%) as a colorless oil. IR (neat) 1739 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ : 6.09 (1H, d, *J*=9.5Hz), 5.63 (1H, dtd, *J*=15.5, 7.0, 1.0 Hz), 5.43 (1H, ddt, *J*=15.5, 7.5, 1.0 Hz), 4.17 (2H, q, *J*=7.0 Hz), 4.02 (1H, ddd, *J*=9.5, 7.5, 1.0 Hz), 2.02 (2H, q, *J*=7.0 Hz), 1.44-1.36 (2H, m), 1.27 (3H, t, *J*=7.0 Hz), 0.89 (3H, t, *J*=7.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ : 170.9, 134.6, 126.3, 123.8, 122.5, 61.3, 49.6, 34.4, 22.1, 14.1, 13.5. HRMS (CI) *m/z* : Calcd for $C_{11}H_{17}Cl_2O_2$ $[M+H]^+$ 251.0604. Found : 251.0593.

Ethyl (*E*)-2-(2,2-Dichloroethenyl)-3-undecenoate (11d)

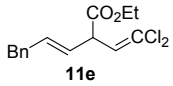


11d

Me_2Zn (1.0 M in hexane, 0.3 mL, 0.3 mmol) was added eight times at 1 h intervals to a solution of **1d** (66.6 mg, 0.3 mmol) in $CHCl_3$ (1.0 mL) under nitrogen atomosphere at rt. After being stirred at the same temperature for 24 h, the reaction mixture was diluted with sat. NH_4Cl and extracted with $CHCl_3$. The organic phase was dried over $MgSO_4$ and concentrated at reduced pressure. The residue was purified by preparative TLC (hexane : AcOEt = 20 : 1) to afford **11d** (61.5 mg, 74 %) as a colorless oil. IR (neat) 1729 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ : 6.09 (1H, d, *J*=9.0Hz), 5.77 (1H, dtd, *J*=15.0, 6.5,

1.0 Hz), 5.42 (1H, ddt, *J*=15.0, 7.0, 1.5 Hz), 4.17 (2H, q, *J*=7.0 Hz), 4.04-3.99 (1H, m), 2.03 (2H, q, *J*=6.5 Hz), 1.41-1.26 (10H, m), 1.27 (3H, t, *J*=7.0 Hz), 0.88 (3H, t, *J*=6.5 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ : 171.0, 135.0, 126.3, 123.6, 122.5, 62.5, 61.3, 49.6, 32.4, 31.8, 29.1, 29.0, 28.9, 22.6, 14.1. HRMS (ESI) *m/z* : Calcd for $C_{15}H_{24}Cl_2O_2Na$ $[M+Na]^+$ 329.1046. Found : 329.1045.

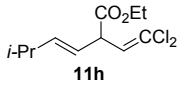
Ethyl (*E*)-2-(2,2-Dichloroethenyl)-5-phenyl-3-pentenoate (11e)



11e

Me_2Zn (1.0 M in hexane, 0.3 mL, 0.3 mmol) was added eight times at 1 h intervals to a solution of **1e** (64.9 mg, 0.3 mmol) in $CHCl_3$ (2.5 mL) under nitrogen atomosphere at rt. After being stirred at the same temperature for 24 h, the reaction mixture was diluted with sat. NH_4Cl and extracted with $CHCl_3$. The organic phase was dried over $MgSO_4$ and concentrated at reduced pressure. The residue was purified by preparative TLC (hexane : AcOEt = 20 : 1) to afford **11e** (59.6 mg, 67%) as a colorless oil. IR (neat) 1737 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.32-7.15 (5H, m), 6.10 (1H, d, *J*=9.0Hz), 5.80 (1H, dtd, *J*=15.0, 6.5, 1.0 Hz), 5.54 (1H, ddt, *J*=15.0, 7.0, 1.0 Hz), 4.17 (2H, q, *J*=7.0 Hz), 4.10-4.04 (1H, m), 3.38 (2H, d, *J*=6.5 Hz), 1.27 (3H, t, *J*=7.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 170.7, 139.5, 133.1, 128.5, 128.3, 126.2, 125.9, 125.3, 122.8, 61.4, 49.4, 38.6, 14.1. HRMS (EI) *m/z* : Calcd for $C_{15}H_{16}Cl_2O_2$ $[M^+]$ 298.0526. Found : 298.0530.

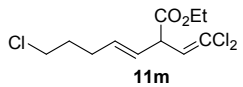
Ethyl (*E*)-2-(2,2-Dichloroethenyl)-5-methyl-3-hexenoate (11h)



11h

Me_2Zn (1.0 M in hexane, 0.3 mL, 0.3 mmol) was added eight times at 1 h intervals to a solution of **1h** (50.5 mg, 0.3 mmol) in $CHCl_3$ (2.5 mL) under nitrogen atomosphere at rt. After being stirred at the same temperature for 24 h, the reaction mixture was diluted with sat. NH_4Cl and extracted with $CHCl_3$. The organic phase was dried over $MgSO_4$ and concentrated at reduced pressure. The residue was purified by preparative TLC (hexane : AcOEt = 20 : 1) to afford **11h** (53.0 mg, 71%) as a colorless oil. IR (neat) 1729 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.10 (1H, d, *J*=9.5 Hz), 5.60 (1H, dd, *J*=15.5, 7.0 Hz), 5.38 (1H, dd, *J*=15.5, 7.0 Hz), 4.17 (2H, q, *J*=7.0 Hz), 4.00 (1H, dd, *J*=9.5, 7.0 Hz), 2.29 (1H, m), 1.27 (3H, t, *J*=7.0 Hz), 0.39 (6H, d, *J*=7.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ : 171.2, 141.9, 126.6, 121.1, 61.5, 49.7, 31.2, 22.3, 14.3. HRMS (ESI) *m/z* : Calcd for $C_{11}H_{17}Cl_2O_2$ $[M+H]^+$ 251.0600. Found : 251.0594.

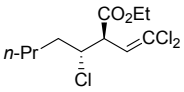
Ethyl (*E*)-7-chloro-2-(2,2-Dichloroethenyl)-3-heptenoate (11m)



11m

Me_2Zn (1.0 M in hexane, 0.3 mL, 0.3 mmol) was added eight times at 1 h intervals to a solution of **1m** (60.2 mg, 0.3 mmol) in $CHCl_3$ (2.5 mL) under nitrogen atomosphere at rt. After being stirred at the same temperature for 24 h, the reaction mixture was diluted with sat. NH_4Cl and extracted with $CHCl_3$. The organic phase was dried over $MgSO_4$ and concentrated at reduced pressure. The residue was purified by preparative TLC (hexane : AcOEt = 20 : 1) to afford **11m** (50.2 mg, 59%) as a colorless oil. IR (neat) 1728 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.10 (1H, d, *J*=9.5 Hz), 5.60 (1H, dt, *J*=16.0, 6.0 Hz), 5.52 (1H, br dd, *J*=16.0, 8.0 Hz), 4.18 (2H, q, *J*=7.0 Hz), 4.03 (1H, dd, *J*=9.5, 8.0 Hz), 3.52 (2H, t, *J*=7.0 Hz), 2.22 (2H, q, *J*=7.0 Hz), 1.88 (2H, quint, *J*=7.0 Hz), 1.29 (3H, t, *J*=7.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ : 170.7, 132.6, 125.9, 125.2, 122.8, 61.5, 49.5, 44.1, 31.6, 29.4, 14.1. HRMS (ESI) *m/z* : Calcd for $C_{11}H_{16}Cl_3O_2$ $[M+H]^+$ 285.0210. Found : 285.0209.

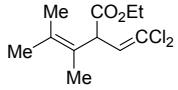
Ethyl *anti*-3-Chloro-2-(2,2-dichloroethenyl)heptanoate (12)



12

To a solution of cyclopropane **6a** (287 mg, 1.0 mmol) in $CHCl_3$ (10 mL) was added Me_2Zn (1.0 M in hexane, 2.0 mL, 2.0 mmol) under nitrogen atmosphere at room temperature. After being stirred at the same temperature for 2 h, the reaction mixture was diluted with sat. NH_4Cl and extracted with $CHCl_3$. The organic phase was dried over Na_2SO_4 and concentrated at reduced pressure. Purification by flash column chromatography (hexane) afforded **12** (266 mg, 93%) as a colorless oil. IR ν_{max} (neat) cm^{-1} : 1738.^{1}H NMR (500 MHz, $CDCl_3$) δ : 6.16 (1H, d, *J*=10.0 Hz), 4.42-4.38 (1H, m), 4.22 (2H, q, *J*=7.0 Hz), 3.72 (1H, dd, *J*=10.0, 4.5 Hz), 1.73-1.69 (2H, m), 1.55-1.52 (2H, m), 1.40-1.27 (2H, m), 1.30 (3H, t, *J*=7.0 Hz), 0.92 (3H, t, *J*=7.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ : 169.2, 124.7, 123.4, 62.4, 61.8, 52.6, 35.8, 28.7, 22.0, 14.1, 13.9. HRMS (CI) *m/z* : Calcd for $C_{11}H_{18}Cl_3O_2$ $[M+H]^+$ 287.0372, Found : 287.0369.

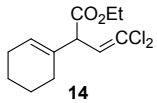
Ethyl (*E*)-2-(2,2-Dichloroethenyl)-3,4-dimethyl-3-pentenoate (13)



13

Me_2Zn (1.0 M in hexane, 0.3 mL, 0.3 mmol) was added four times at 1 h intervals to a solution of **1j** (50.5 mg, 0.3 mmol) in $CHCl_3$ (2.5 mL) under nitrogen atomosphere at rt. After being stirred at the same temperature for 24 h, the reaction mixture was diluted with sat. NH_4Cl and extracted with $CHCl_3$. The organic phase was dried over $MgSO_4$ and concentrated at reduced pressure. The residue was purified by preparative TLC (hexane : AcOEt = 20 : 1) to afford **13** (42.2 mg, 57%) as a colorless oil. IR (neat) 1734 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ : 6.24 (1H, d, *J*=9.5Hz), 4.52 (1H, d, *J*=9.5 Hz), 4.17 (2H, m), 1.82 (3H, br s), 1.71 (3H, s), 1.62 (3H, s), 1.26 (3H, t, *J*=7.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ : 171.2, 130.2, 126.4, 122.4, 121.6, 61.1, 49.5, 21.0, 20.8, 15.0, 14.2. HRMS (EI) *m/z* : Calcd for $C_{11}H_{16}Cl_2O_2$ $[M^+]$ 250.0526. Found : 250.0524.

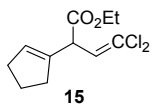
Ethyl 4,4-dichloro-2-(1-cyclohexenyl)-3-butenoate (14)



14

Me_2Zn (1.0 M in hexane, 0.3 mL, 0.3 mmol) was added six times at 1 h intervals to a solution of **1g** (54.1 mg, 0.3 mmol) in $CHCl_3$ (2.5 mL) under nitrogen atomosphere at rt. After being stirred at the same temperature for 24 h, the reaction mixture was diluted with sat. NH_4Cl and extracted with $CHCl_3$. The organic phase was dried over $MgSO_4$ and concentrated at reduced pressure. The residue was purified by preparative TLC (hexane : AcOEt = 20 : 1) to afford **14** (42.7 mg, 55%) as a colorless oil. IR (neat) 1735 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ : 6.19 (1H, d, *J*=10.0 Hz), 5.63 (1H, m), 4.17 (2H, q, *J*=7.0 Hz), 3.94 (1H, d, *J*=10.0 Hz), 2.05-2.02 (2H, m), 2.00-1.96 (2H, m), 1.75-1.71 (1H, m), 1.69-1.53 (3H, m), 1.27 (3H, t, *J*=7.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ : 170.8, 133.2, 126.5, 125.9, 122.0, 61.2, 53.8, 26.7, 25.3, 22.7, 21.9, 14.1. HRMS (ESI) *m/z* : Calcd for $C_{12}H_{16}Cl_2O_2Na$ $[M+Na]^+$ 285.0420. Found : 285.0426.

Ethyl 4,4-dichloro-2-(1-cyclopentenyl)-3-butenoate (15)

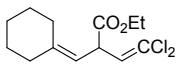


15

Me_2Zn (1.0 M in hexane, 0.3 mL, 0.3 mmol) was added eight times at 1 h intervals to a solution of **1n** (49.4 mg, 0.3 mmol) in $CHCl_3$ (2.5 mL) under nitrogen atomosphere at rt. After being stirred at the same temperature for 24 h, the reaction mixture was diluted with sat. NH_4Cl and extracted with $CHCl_3$. The organic phase was dried over $MgSO_4$ and concentrated at reduced pressure. The residue was purified by preparative TLC (hexane : AcOEt = 20 : 1) to afford **15** (39.8 mg, 54%) as a colorless oil. IR (neat) 1731 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ : 6.19 (1H, d, *J*=10.0 Hz), 5.59 (1H, m), 4.18 (2H, q, *J*=7.0 Hz), 4.19-4.15 (1H, m), 2.40-2.26 (4H, m), 1.95-1.84 (2H, m), 1.28 (3H, t, *J*=7.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ : 170.3, 138.2, 128.3, 126.0, 122.3, 61.3, 48.5, 33.4, 32.3, 23.0, 14.1. HRMS (ESI) *m/z* : Calcd for $C_{11}H_{14}Cl_2O_2Na$ $[M+Na]^+$ 271.0263. Found : 271.0264.

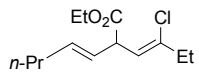
Ethyl (*E*)-4,4-dichloro-2-(cyclohexylidenemethyl)-3-butenoate (16)



16

Me_2Zn (1.0 M in hexane, 0.3 mL, 0.3 mmol) was added eight times at 1 h intervals to a solution of **1o** (57.7 mg, 0.3 mmol) in $CHCl_3$ (2.5 mL) under nitrogen atomosphere at rt. After being stirred at the same temperature for 24 h, the reaction mixture was diluted with sat. NH_4Cl and extracted with $CHCl_3$. The organic phase was dried over $MgSO_4$ and concentrated at reduced pressure. The residue was purified by preparative TLC (hexane : AcOEt = 20 : 1) to afford **16** (48.0 mg, 58%) as a colorless oil. IR (neat) 1736 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ : 6.07 (1H, d, *J*=9.0 Hz), 5.06 (1H, br d, *J*=9.0 Hz), 4.29 (1H, t, *J*=9.0 Hz), 4.15 (2H, q, *J*=7.0 Hz), 2.23 (2H, br), 2.10 (2H, br), 1.88-1.50 (6H, m), 1.27 (3H, t, *J*=7.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ : 171.3, 144.8, 127.2, 121.7, 115.2, 61.2, 45.3, 37.0, 29.5, 28.4, 27.7, 26.6, 14.1. HRMS (ESI) *m/z* : Calcd for $C_{13}H_{19}Cl_2O_2$ $[M+H]^+$ 277.0757. Found : 277.0750.

Ethyl (3*E*)-2-[(1*Z*)-2-Chloro-1-buten-1-yl]-3-heptenoate (S1)



S1

To a solution of **11a** (100 mg, 0.40 mmol) and Pd(dpephos) (14.3 mg, 0.02 mmol, 5 mol%) in DMF (3 mL) was added Et_2Zn (1.0 M in hexane, 0.96 mL, 0.96 mmol) under argon atmosphere at room temperature. After being stirred at the 50 °C for 3 h, the reaction mixture was diluted with HCl and extracted with Et_2O. The combined organic phase was washed with sat. NaCl, dried over $MgSO_4$ and concentrated at reduced pressure. Purification of the residue by flash column chromatography (hexane : AcOEt = 20 : 1) afforded **S1** (63.4 mg, 65%) as a colorless oil. The geometry was deduced from NOESY experiments IR (neat) cm^{-1} : 1737. ^{1}H NMR (500 MHz $CDCl_3$) δ : 5.68 (1H, dt, *J*=9.0, 1.5 Hz), 5.60 (1H, ddt, *J*=15.5, 7.0, 1.5 Hz), 5.45 (1H, ddt, *J*=15.5, 7.0, 1.5 Hz), 4.17-4.13 (1H, m), 4.15 (2H, q, *J*=7.0 Hz), 2.40-2.36 (2H, m), 2.00 (2H, br q, *J*=7.0 Hz), 1.39 (2H, q, *J*=7.0 Hz), 1.26 (3H, t, *J*=7.0 Hz), 1.14 (3H, t, *J*=7.5 Hz), 0.88 (3H, t, *J*=7.0 Hz). ^{13}C NMR (125 MHz) δ : 175.0, 141.1, 136.0, 127.9, 123.6, 63.6, 51.3, 37.1, 35.5, 24.8, 16.8, 16.2, 15.1. HRMS (EI) *m/z* : Calcd for $C_{13}H_{21}ClO_2$ $[M^+]$ 244.1229. Found : 244.1220.

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1) P. Muller, C. Granicher, *Helv. Chim. Acta*., 1993, **76**, 521.

2) E. E. Wyatt, S. Fergas, W. R. J. D. Galloway, A. Bender, D. J. Fox, A. T. Plowright, A. S. Jessiman, M. Welch, D. R. Spring, *Chem. Commun*., 2006, 3296.