# Convenient synthesis of new functionalized cyclopropanes from monoterpenic olefines

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**Abstract**
Five new cyclopropyl-ketoacids were prepared in good yields from monoterpenic olefines using solid-liquid phase transfer catalysis (SL-PTC) dichlorocyclopropanation reaction followed by oxidative cleavage with $RuCl_3$-$NaIO_4$ system. The nonchlorinated cyclopropanes were obtained by sodium/methanol reduction of the corresponding *gem*-dichlorocyclopropanes.

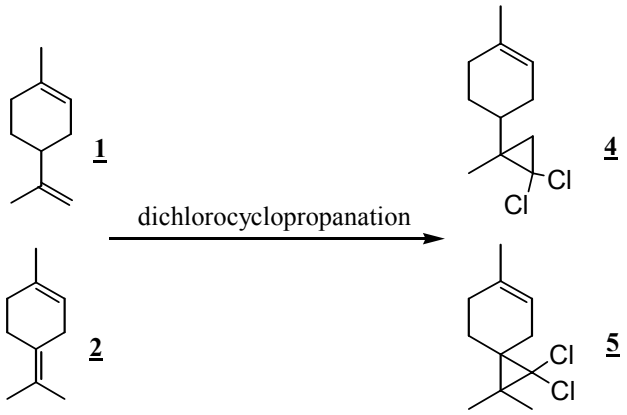
**Keywords :** monoterpenes, cyclopropyl-ketoacids, phase transfer catalysis, oxidative cleavage

## Introduction

The enormous importance of functionalized cyclopropanes, in various scientific fields, lies in their diverse biological activity[1] and their usefulness as valuable building blocks in organic synthesis.[2] Recently[3-5], we have reported the synthesis of new functionalized cyclopropanes from terpenic olefins. This synthesis involves a periselective *gem*-dihalocyclopropanation reaction (under SL-PTC conditions)[6] of one of the terpenic olefine double bounds followed by an oxidative cleavage of the other, using $RuCl_3$-$NaIO_4$ catalytic system.[7] This facile and convenient methodology has been adapted for the preparation of five new cyclopropyl-ketoacids which are reported herein.

## Results and discussion

Three monoterpenes were selected as starting materials : limonene **1**, terpinolene **2** and γ-terpinene **3**. We notice here that for **1** and **2**, our strategy consists in a dichlorocyclopropanation of the exocyclic double bound (Scheme 1), before the oxidative cleavage of the internal one.




**Scheme 1**

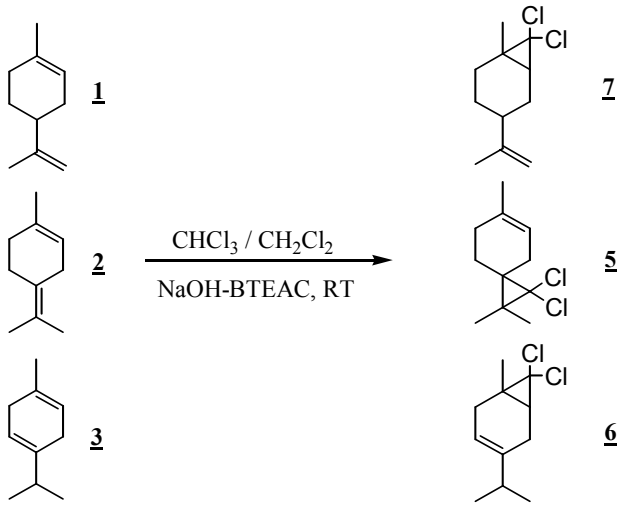
The dichlorocyclopropanation reaction was achieved using phase-transfer catalysis technique. The primary advantages of using phase-transfer catalysis are to obtain a large conversion, high reaction rate and selectivity at moderate reaction conditions. [8-10] It is interesting to note that powdered KOH or NaOH/BTEAC/$CHCl_3$ has been suggested as a very effective $CCl_2$ precursor.[11] A comparison with the original Makosza method showed similar yields, but the process with solid base was proved to be faster.[10-11]

Earlier[12], Sirovski and al. have published the work discussing various models of phase-transfer catalysed reactions in the different solid/liquid systems. It was shown that Makosza reaction in this system is hindered by the formation of the crust of NaCl.

A suggestion was put forward that phase-transfer catalysed reactions in these systems closely resemble to the so-called topochemical processes (solid/fluid) described elsewhere.[13]

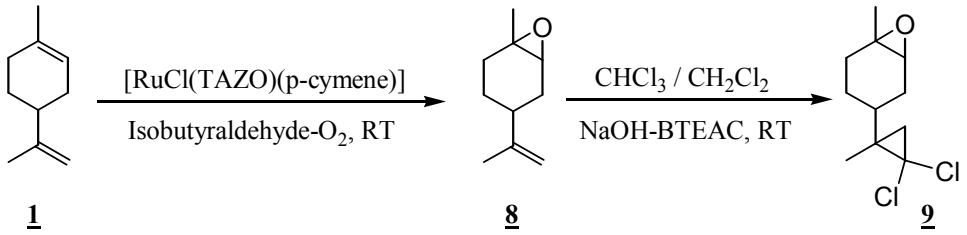
For this reason, we have studied the cyclopropanation reaction of limonene **1**, terpinolene **2** and γ-terpinene **3** under controlled solid/liquid phase transfer catalysis conditions. Dichlorocarbene was used as the carbene component. It was generated by the adapted method to terpenic olefins[14], i.e., reaction of powdered NaOH with chloroform at room temperature in the presence of benzyltriethylammonium chloride (BTEAC) as the phase transfer catalyst. We found that **2** and **3** afforded the desired *gem*-dichlorocyclopropanes **5** (71%) and **6** (74%), respectively, while limonene **1** led to the nondesired product **7**[15] (62%) as a mixture of cis/trans stereoisomers in which the internal double bound was affected (Scheme 2). We notice here, that despite the variation of the experimental parameters such as phase transfer catalysts, catalyst amount,

sodium hydroxide concentration and temperature, the dichlorocarbene addition reaction to limonene **1** always gives the nondesired product **7**[15].




**Scheme 2**

In order to direct the dichlorocyclopropanation reaction towards the exocyclic double bound, **1** was first epoxidized under aerobic epoxidation conditions described recently[16]. The resulting epoxylimonene **8**[16], obtained as cis/trans (40/60) diastereomeric mixture in 91 % yield, was then treated with dichlorocarbene (generated in-situ under the same conditions described above) to provide the diclorocyclopropane **9**[17] in 90 % yield, as a mixture of four stereoisomers (two faces of the double bond in **8** are likely not sterically equivalent) (Scheme 3).




**Scheme 3**

All the obtained products **5-9** were fully characterised by their mass and NMR spectroscopic data.

In order to obtain the nonchlorinated cyclopropanes, we reduced compounds **5**, **6** and **9** using metallic sodium in methanol. The reaction afforded, in excellent yields, the corresponding cyclopropanes **10** (92%), **11** (95%) and **12** (97%)[17] respectively (Scheme 4). The compound **12** was also isolated as a cis/trans (31/69) diastereomeric mixture.

Before oxidation of obtained cyclopropanes **10**, **11** and **12**, we have first checked the oxidative cleavage reaction on compound **12** in order to optimize the reaction conditions. Table 1 summarises some representative results obtained with **12** using freshly prepared $RuO_4$ as catalyst and $NaIO_4$ (stoichoimetric) as oxidant.

**Table 1**: Oxidative cleavage of **12** using the system $RuCl_3$-$NaIO_4$.

| Entry | S/C[b] | $NaIO_4$ (eq. number) | Time (h) | **15** yield (%) |
|---|---|---|---|---|
| 1 | 50 | 10 | 30 | 87 |
| 2 | 50 | 8 | 30 | 85 |
| 3 | 50 | 4 | 62 | 42 |
| 4 | 50 | 2 | 62 | 05 |
| 5 | 100 | 8 | 48 | 71 |
| 6 | 500 | 8 | 48 | 10 |

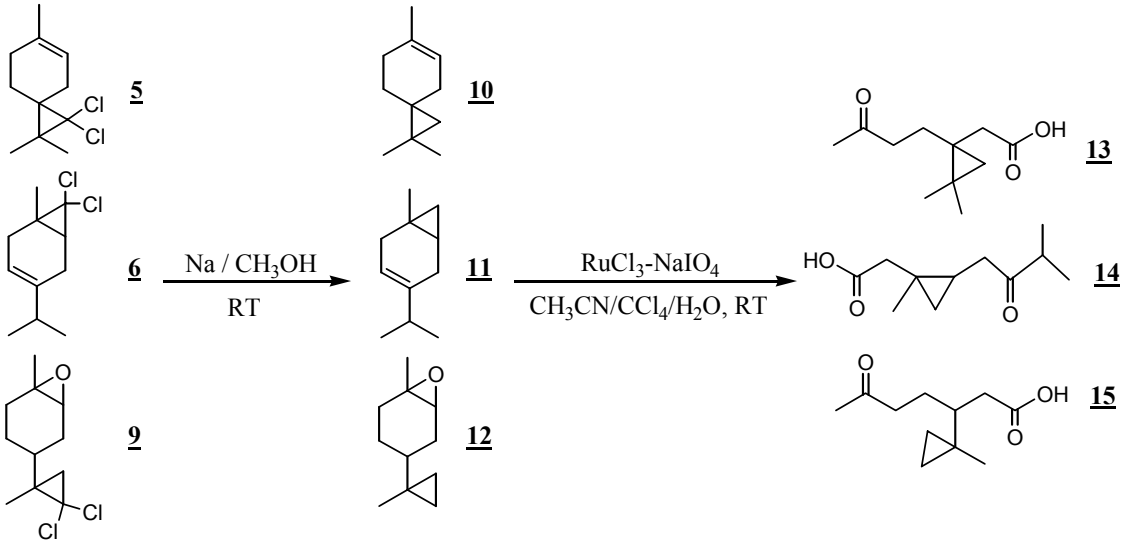
[a]Conditions: **12** = 3.1 mmol; $H_2O$ =6 mL; $CH_3CN$ = 4 mL; $CCl_4$ = 4 mL; Temperature =20 °C;
[b] S/C = substrate/catalyst.

Compound **12** was readily cleaved to the corresponding ketoacid **15** with high yield (Table 1 entry 1-2) by quenching the reaction after 30 hours (Scheme 4).

An increase of the substrate/catalyst ratio (100 instead 50) led as expected to a slower reaction but interestingly high yield into the acid. With a substrat/catalyst ratio 500, only 10% of ketoacid **15** were obtained after 48 hours (entry 6). On the other hand a decrease in the $NaIO_4$/substrate ratio had a very detrimental effect on conversion (entry 4). The best result (85% yield) was obtained at room temperature after 30 hours with 8 equivalent of $NaIO_4$ and substrate/catalyst ratio 50 (entry 2).

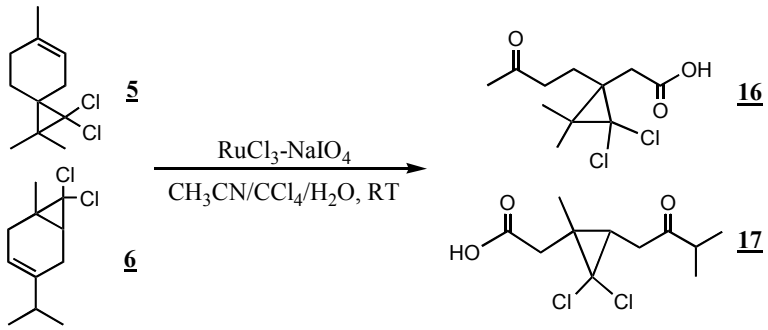
Under optimised conditions (8 equivalent of $NaIO_4$, substrate/catalyst ratio 50, room temperature), oxidative cleavage of cyclopropanes **10** and **11** with $RuCl_3$-$NaIO_4$ system afforded quantitatively the corresponding cyclopropyl-ketoacids **13** (81%) and **14** (78%) (Scheme 4). We notice here that the stereochemistry of **14** at the cyclopropane must be Z since it originates from **11**.

The spectroscopic data of the three newly prepared cyclopropyl-ketoacids **13**, **14** and **15** are consistent with the assigned structures, mainly characterized by $^1$H NMR spectroscopy; the signals for cyclopropanic protons are ranged between 0.1-0.6 ppm and the signals for ethylenic protons disappeared. Their $^{13}$C NMR spectra reveal carbonyl groups resonance at about 209-213 ppm (ketone carbonyl group) and 178-179 ppm (acid carbonyl group).




**Scheme 4**

Under identical conditions dichlorocyclopropyl-ketoacids **16** and **17** were similarly prepared by oxidative cleavage of the corresponding precursors **5** and **6** (Scheme 5).




**Scheme 5**

Their spectroscopic data are in full accordance with the attributed structures which were mainly characterized by $^{13}C$ NMR spectroscopy. The cyclopropanic $CCl_2$ groups appeared at 70-75 ppm, whereas acid and ketone carbonyl groups signals revealed at 176 ppm and 208-212 ppm respectively.

## Conclusion

We have described a simple and convenient synthesis of new cyclopropyl-ketoacids starting from limonene, terpinolene and γ-terpinene. The nonchlorinated cyclopropyl-ketoacids **13-15** were prepared by a periselective dichlorocyclopropanation reaction (under SL-PTC conditions)

of the corresponding monoterpenes followed by a sodium/methanol reduction of the *gem*-dichlorocyclopropanes **5**, **6** and **9**. The oxidative cleavage of the obtained cyclopropanes **10-12** with system $RuCl_3$-$NaIO_4$, afforded the desired cyclopropyl-ketoacids **13-15** in 53-67 % overall yields. It is worth mentioning that in the case of limonene, we were compelled to epoxidize the internal double bound in order that the ensuing dichlorocyclopropanation reaction would occur at the exocyclic one. The dichlorocyclopropyl-ketoacids **16** and **17** were similarly obtained *via* a direct oxidative cleavage from the corresponding precursors **5** and **6** in 56% and 62 % overall yields, respectively.

## Experimental Section

**General.** All reagents and solvents were purchased from commercial sources (Aldrich, 112 Acros) and used as received. The reaction mixtures were analysed on a Trace 2000 series chromatograph equipped with an FID detector, using silica capillary columns CPSil5CB (10 m × 0.33 mm, Chrompack). Column chromatography was performed on silica gel (Merck 60, 220-440 mesh). A BP5 (25 m × 0.25 mm) capillary column was used for GC/MS coupled analyses with a Saturn 2000 spectrometer. $^1$H NMR and $^{13}$C NMR spectra were recorded on a Bruker Model AVANCE 300 using $CDCl_3$ as the solvent and $SiMe_4$ as the internal standard.

**Dichlorocyclopropanation**:

At 0°C 3.00 g (75 mmol) of sodium hydroxide was added to 6.00 mL (74 mmol) of chloroform and 0.02 g (0.1mmol) of benzyltriethylammonium chloride (BTEAC) in 6 mL of dichloromethane. The mixture was stirred for 10 min, then 0.86 g (6.3 mmol) of the monoterpene was added dropwise over a period of 30 min. The mixture was strirred for 8 h at 25 °C and then hydrolyzed by addition of 20 mL of water. The organic layer was separated and the aqueous layer was washed three times with 10 mL of dichloromethane. The combined organic extracts were dried over $Na_2SO_4$ and concentrated under reduced pressure. The residue was then subjected to purification by silica gel column chromatography (hexane) to afford the corresponding *gem*-dichlorocyclopropane as colorless oils.

**1,1-Dichloro-2,2,6-trimethyl-spiro[2.5]oct-5-ene (5)**. Yield : 71%; m/z : 223 (0.55 %, MH+4$^+$) ; 221 (3.34 %, MH+2$^+$) ; 219 (5.17 %, MH$^+$); $^1$H NMR ($CDCl_3$): δ = 1.20 (s, 3H), 1.30 (s, 3H), 1.50-1.70 (m, 2H), 1.75 (s, 3H), 1.80-2.40 (m, 4H), 5.40 (br s, 1H); $^{13}$C NMR ($CDCl_3$): δ = 18.9 ($CH_3$), 19.1 ($CH_3$), 22.9 ($H_2C8$), 25.7 ($CH_3$), 28.7 ($H_2C7$), 29.2 ($H_2C4$), 32.8 (C2), 33.6 (C3), 67.0 ($Cl_2C1$), 119.1(HC5), 134.7 (C6).

**7,7-Dichloro-4-isopropyl-1-methyl-bicyclo[4.1.0]hept-3-ene (6)**. Yield : 74 %; m/z : 223 (3.25 %, MH+4$^+$) ; 221 (20.71 %, MH+2$^+$) ; 219 (33.72 %, MH$^+$); $^1$H NMR ($CDCl_3$): δ = 0.98 (d, J = 6.9 Hz, 6H), 1.05 (dd, J = 14.1, 7.9 Hz, 1H), 1.44 (s, 3H), 2.00-2.50 (m, 5H), 5.26 (br s, 1H); $^{13}$C NMR ($CDCl_3$): δ = 20.9 ($H_2C5$), 21.2 ($CH_3$), 21.3 ($CH_3$), 24.4 ($CH_3$), 28.7 ($H_2C2$), 30.8 (C1), 31.6 (H<u>C</u>($CH_3$)$_2$), 34.8 (HC6), 72.2 ($Cl_2C7$), 115.5(HC3), 138.7 (C4).

**4-(2',2'-Dichloro-1'-methylcyclopropyl)-1-methyl-7-oxabicyclo[4.1.0]heptane (9)**. Obtained as an inseparable diastereomeric mixture.Yield : 90 %; m/z : 239(0.35 %, MH+4$^+$) ; 237 (2.12

%, MH+2$^{+}$) ; 235 (3.28 %, MH$^{+}$); $^{1}$H NMR ($CDCl_3$): δ = 1.05 (s, 2.1H, major diastereoisomers), 1.06 (s, 0.9H, minor diastereoisomers), 0.91-1.20 (m, 2H), 1.23 (s, 3H), 1.28-1.63(m, 4H), 1.73 (d, J = 14.3, 0.3H, minor diastereoisomers),1.76 (d, J = 14.2, 0.7H, major diastereoisomers), 2.05 (m, 1H), 2.08 (m, 0.7H, major diastereoisomers), 2.10 (m, 0.3H, minor diastereoisomers), 2.93 (d, J = 5.2 Hz, 0.7H, major diastereoisomers), 2.95 (m, 0.3H, minor diastereoisomers); $^{13}$C NMR ($CDCl_3$): δ = 15.6 and 15.7 ($CH_3$), 22.9 and 25.4 ($H_2C5$), 23.0 ($CH_3$), 26.1 and 27.9 ($H_2C3$), 29.4 and 30.8 ($H_2C3'$), 32.7 and 32.8 ($H_2C6$), 31.6 and 33.1 (C1'), 36.1 and 40.0 (HC4), 57.4 and 57.7 (C1), 59.0 and 60.4 (HC2), 68.0 and 68.7 ($Cl_2C2'$).

**Reduction of *gem*-dichlorocyclopropanes (general procedure).** To a cooled ( 0°C) solution of 9.2 mmol of the dichlorocyclopropane in 50 mL of ether were added, simultaneously over a 1-hour period, 6 g ( 260.86 mmol) of sodium and 30 ml methanol (98 %). The mixture was stirred for 3-hours and another portion of 2 g (87 mmol) of sodium and 20 mL of methanol (98 %) were added. Stirring was maintained overnight at room temperature. The mixture was diluted with water and poured into a separatory funnel. The layers were separated and the aqueous phase was extracted with ether. The combined organic layers were dried over anhydrous magnesium sulfate, filtered and concentrated by rotary evaporation. The residue was chromatographied on silica gel column using pentane as the eluent. The corresponding cyclopropanes were obtained as colorless oils.

**1,1,6-Trimethyl-spiro[2.5]oct-5-ene (10)**. Yield : 92 %; m/z : 151 (7.87 %, MH$^{+}$); $^{1}$H NMR ($CDCl_3$): δ = 0.09 (d, J = 7.1 Hz, 1H), 0.14 (d, J = 7.1 Hz, 1H), 1.16 (s, 3H), 1.18 (s, 3H), 1.70 (s, 3H), 1.91 (m, 2H), 2.10 (m, 2H), 2.33 (m, 2H), 5.15 (br s, 1H); $^{13}$C NMR ($CDCl_3$): δ = 17.2 (C1), 19.0 ($CH_3$), 21.9 ($CH_3$), 23.6 ($CH_3$), 25.8 ($H_2C2$), 28.1 ($H_2C7$), 30.1 ($H_2C4$), 32.1 ($H_2C8$), 37.2 (C3), 121.3 (HC5), 134.3 (C6).

**4-Isopropyl-1-methyl-bicyclo[4.1.0]hept-3-ene (11)**. Yield : 95 %; m/z : 151 (56.56 %, MH$^{+}$); $^{1}$H NMR ($CDCl_3$): δ = 0.18 (m, 2H), 0.80 (m, 1H), 0.95 (s, 3H), 0.97 (s, 3H),1.09 (s, 3H), 1.31 (m, 2H), 2.25 (m, 2H), 2. 31 (m, 1H), 5.22 (br s, 1H); $^{13}$C NMR ($CDCl_3$): δ = 13.1 ($H_2C7$), 14.8 (HC6), 18.9 ($CH_3$), 21.4 ($CH_3$), 23.1 (C1), 26.0 ($H_2C5$), 27.6 ($CH_3$), 31.4 ($H_2C5$), 35.2 ($HC(CH_3)_2$), 115.8 (HC3), 139.9 (C4).

**1-Methyl-4-(1'-methylcyclopropyl)-7-oxabicyclo[4.1.0]heptane (12)**. Obtained as cis/trans 31/69 diastereomeric mixture.Yield : 97 %; m/z : 167 (8.20 %, MH$^{+}$); $^{1}$H NMR ($CDCl_3$): δ = 0.10 (br s, 4H), 0.79 (s, 3H), 1.20 (s, 3H), 1.41-1.99 (m, 7H), 2.88 (d, J = 5.4 Hz, 0.7H, trans diastereoisomer), 2.95 (br s, 0.3H, cis diastereoisomer); $^{13}$C NMR ($CDCl_3$): δ = 12.4 and 12.5 ($H_2C2'$, $H_2C3'$), 18.3 and 18.5 (C1'), 18.8 and 18.9 ($CH_3$), 23.1 and 25.6 ($H_2C3$), 23.2 and 24.6 ($CH_3$), 27.6 and 29.5 ($H_2C5$), 29.1 and 31.1 ($H_2C2$), 37.3 and 41.7 (HC4), 57.6 and 57.8 (C1), 59.6 and 61.3 (HC6).

**Oxidative cleavage (general procedure).** In a typical procedure, water (6 mL), periodic acid (5.67 g, 24.8 mmol) and NaOH (0.99 g, 24.8 mmol) were introduced in a three necked flask equipped with a magnetic stirrer bar. The mixture was stirred and cooled at 0 °C (ice bath). Then, at this temperature were successively added $CCl_4$ (4 mL), $CH_3CN$ (4 mL) and $RuCl_3 \times 3H_2O$ (0.0165 g, 0.063 mmol). After 15 min, the substrate (0.422 g, 3.1 mmol) was added. The ice bath

was removed and the reaction, conducted at room temperature, was monitored by gas chromatography of samples taken at regular time intervals. At the end of the reaction, 25 mL of $CHCl_3$ were added, and the organic layer was washed, dried ($MgSO_4$), filtered on silica gel in order to remove the precipitated $RuO_4$ and then concentrated to give the corresponding cyclopropyl-ketoacids.

**[2,2-Dimethyl-1-(3'-oxobutyl)-cyclopropyl]-acetic acid (13)**. Yield : 81 % ; mp 94-95 °C (hexane / ether 1:1); m/z : 199 (55.74 %, $MH^+$); $^1H$ NMR ($CDCl_3$): δ = 0.20 (d, J = 4.4 Hz, 1H), 0.25 (d, J = 4.4 Hz, 1H), 1.07 (s, 3H), 1.09 (s, 3H), 1.70 (m, 2H), 2.09 (s, 3H), 2.23 (m, 2H), 2.49 (m, 2H); $^{13}C$ NMR ($CDCl_3$): δ = 15.1 ($CH_3$), 20.7 (C2), 21.9 ($CH_3$), 24.6 (C1), 25.6 ($H_2C3$), 27.2 ($H_2C1'$), 29.9 ($CH_3$), 37.5 ($H_2C2'$), 41.5 ($H_2C$-COOH), 178.2 (COOH), 209.2 (C3').

**(Z) [1-Methyl-2-(3'-methyl-2'-oxobutyl)-cyclopropyl]-acetic acid (14)**. Yield : 78 % ; viscous oil; m/z : 199 (75.64 %, $MH^+$); $^1H$ NMR ($CDCl_3$): δ = 0.10 (m, 2H), 0.59 (m, 1H), 0.97 (s, 3H), 0.99 (s, 3H), 1.06 (s, 3H), 2.44 (br s, 2H), 2.46-2.55 (m, 3H); $^{13}C$ NMR ($CDCl_3$): δ = 15.3 ($CH_3$), 18.2 ($H_2C3$), 18.7 ($CH_3$), 24.8 ($CH_3$), 33.6 (HC2), 40.3 (HC3'), 40.9 ($H_2C$-COOH), 43.9 (C1), 48.1 ($H_2C1'$), 178.2 (COOH), 213.8 (C2').

**3-(1'-Methylcyclopropyl)-6-oxoheptanoic acid (15)**. Yield : 85 % , visquous oil; m/z : 199 (33.61 %, $MH^+$); $^1H$ NMR ($CDCl_3$): δ = 0.25 (m, 4H), 0.85 (s, 3H), 1.63 (q, J = 7.8 Hz, 2H), 2.09 (s, 3H), 2.10-2.50 (m, 5H); $^{13}C$ NMR ($CDCl_3$): δ = 12.2 ($H_2C2'$), 14.7 ($H_2C3'$), 17.7 ($CH_3$), 18.0 (C1'), 26.9 ($H_2C4$), 29.9 ($CH_3$), 38.4 ($H_2C2$), 41.7 ($H_2C5$), 43.0 (HC3), 179.3 (C1), 209.2 (C6).

**[2,2-Dichloro-3,3-dimethyl-1-(3'-oxobutyl)-cyclopropyl]-acetic acid (16)**. Yield : 79 % ; 104-105 °C (hexane / ether 1:1); m/z : 271 (0.66 %, $MH+4^+$) ; 269 (6.23 %, $MH+2^+$) ; 267 (9.84 %, $MH^+$); $^1H$ NMR ($CDCl_3$): δ = 1.30 (s, 3H), 1.32 (s, 3H), 1.98 (m, 2H), 2.18 (s, 3H), 2.55 (m, 2H), 2.70 (m, 2H); $^{13}C$ NMR ($CDCl_3$): δ = 19.0 ($CH_3$), 20.1 ($CH_3$), 23.6 ($H_2C1'$), 30.0 ($CH_3$), 31.3 (C2), 33.1 (C1), 34.3 ($H_2C$COOH), 40.1 ($H_2C2'$), 75.4 ($Cl_2C3$), 176.7 (COOH), 208.0 (C3).

**(Z) [2,2-Dichloro-1-methyl-3-(3'-methyl-2'-oxobutyl)-cyclopropyl]-acetic acid (17)**. Yield : 83 %; 191-192 °C (hexane / ether 1:1); m/z : 271 (9.84 %, $MH+4^+$) ; 269 (54.10 %, $MH+2^+$) ; 267 (100 %, $MH^+$); $^1H$ NMR ($CDCl_3$): δ = 1.06 (d, J = 6.9 Hz, 3H), 1.07 (d, J = 6.9 Hz, 3H), 1.43 (s, 3H), 1.69 (t, J= 6.9 Hz, 1H), 2.48 (br s, 2H), 2.58-2.72 (m, 3H); $^{13}C$ NMR ($CDCl_3$): δ = 18.1 ($CH_3$), 18.3 ($CH_3$), 22.1 ($CH_3$), 29.1 (C1), 33.6 (HC3), 36.4 ($H_2C$COOH), 37.3 ($H_2C1'$), 40.7 (HC3'), 69.8 ($Cl_2C2$), 176.5 (COOH), 211.9 (C2').

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17. The cis/trans diastereomeric mixture was used in the next reaction without separation.