Convenient Synthesis of Ethenylcyclopropane and Some 2-Cyclopropylcyclopropane Derivatives[1]

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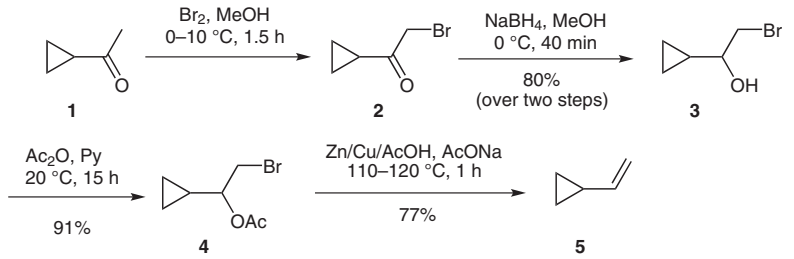
Abstract: Ethenylcyclopropane (**5**) was prepared from cyclopropyl methyl ketone (**1**) in four simple, easily scalable steps (bromination, reduction to the bromohydrin, acetylation of the latter, and reductive elimination with Zn/Cu) in an overall yield of 56%. 1-Bromo-2-cyclopropylcyclopropane (**7**) (approximately 1:1 mixture of *cis*- and *trans*-**7**) was prepared from **5** via the dibromide **6**, and from **7** the boronate *cis*/*trans*-**8** (ratio 1:1) was obtained in 96% yield. Rhodium(II)-catalyzed cyclopropanation of **5** with ethyl diazoacetate gave ethyl 2-cyclopropylcyclopropanecarboxylate (*cis*/*trans*-**9**, ratio 1:1.4) in 80% yield. The latter was also prepared in 79% overall yield by sequential cyclopropanation of buta-1,3-diene with ethyl diazoacetate [under $Rh_2(OAc)_4$ catalysis] and diiodomethane/diethylzinc/trifluoroacetic acid. Curtius degradation of 2-cyclopropylcyclopropanecarboxylic acid (obtained by hydrolysis of the ester) gave 2-cyclopropylcyclopropanamine (1:1.2 mixture of *cis*- and *trans*-isomers) in 58% yield.

Key words: bromination, reduction, elimination, alkenes, cyclopropanation, small rings



Scheme 1 Four-step preparation of ethenylcyclopropane (**5**) from cyclopropyl methyl ketone (**1**)

Introduction

Ethenylcyclopropanes are important structural units in various biologically active natural products[2] as well as composite multifunctional construction units, e.g. for the creation of cyclopentene[3] and oligocyclopropyl derivatives,[4] which have gained considerable importance in recent years.[5] The unsubstituted building block ethenylcyclopropane (**5**), nonsystematically also called vinylcyclopropane, has been prepared in a number of ways,[6] the best of which is by Hofmann elimination from (1-cyclopropylethyl)trimethylammonium hydroxide.[6a] The latter can be prepared in five steps from cyclopropyl methyl ketone (**1**), the overall yield of **5** in this six-step sequence is approximately 30%. For the preparation of bicyclopropyl[7] and various 2-substituted cyclopropylcyclopropane derivatives[8] including 2-cyclopropylcyclopropanamine,[9] we came upon the necessity of making ethenylcyclopropane (**5**) as a precursor available in multigram quantities from inexpensive starting materials. Here is the result of our endeavor.

Results and Discussion

Bromination of cyclopropyl methyl ketone (**1**) in methanol under standard conditions gave the α-bromo ketone **2**[10] and its reduction with sodium borohydride in methanol[11] furnished the bromohydrin **3** (80% yield over two steps),[10] which was treated with acetic anhydride in pyridine to give the vicinal bromoacetoxy derivative **4** (91%) (Scheme 1). Reductive elimination in **4** was brought about with copper-activated zinc (zinc-copper couple) and gave ethenylcyclopropane (**5**) in 77% yield. The overall yield in this four-step sequence obtained in several runs was around 56%. The sequence is easily scal-

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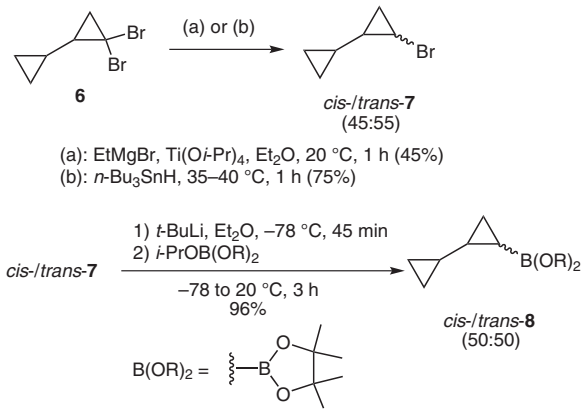
able and requires only inexpensive reagents. In length this sequence is comparable to or shorter than most of the known procedures for the preparation of **5**,[6] and all of the required substrates and reagents are conveniently handled.

Ethenylcyclopropane (**5**) is a suitable precursor to various 2-cyclopropylcyclopropane derivatives, which have become relevant entities in recent years.[5,12] For example, dibromocarbene addition to **5** furnishes 2,2-dibromobicyclopropyl (**6**)[13] in 82% yield,[4b] and the latter can be reduced to a mixture of the diastereomeric monobromides *cis*-**7** and *trans*-**7** (ratio 45:55) with ethylmagnesium bromide in the presence of titanium tetraisopropoxide (45% yield)[14] or tri-*n*-butyltin hydride (75% yield) (Scheme 2).[15] Bromine–lithium exchange on *cis*/*trans*-**7** under conditions as previously published for 1-bromobicyclopropyl,[16] and subsequent trapping of the 2-lithiobicyclopropyl with isopropyl pinacol borate produced the 2-cyclopropylcyclopropaneboronate *cis*/*trans*-**8** (ratio 1:1, 96%). The latter can be employed in Suzuki cross-coupling reactions, as has been shown for the pure *trans*-diastereomer *trans*-**8** prepared along a different route.[8c]

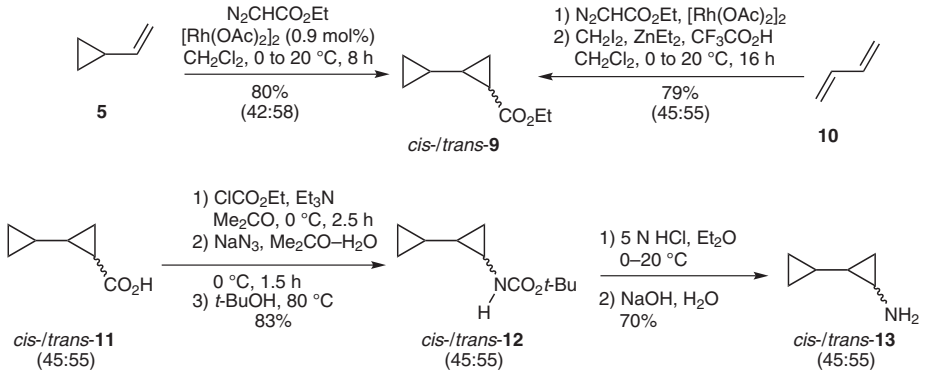


Scheme 2 Preparation of and bromine–lithium exchange on 2-bromobicyclopropyl *cis*/*trans*-**7** with subsequent electrophilic substitution

The most straightforward approach to a dibenzyl-protected 2-cyclopropylcyclopropanamine would be by direct (dibenzylamino)cyclopropanation of ethenylcyclopropane (**5**) with dibenzylformamide in the presence of methyltitanium triisopropoxide and cyclohexylmagnesium bromide, as previously developed for a wide range of alkenes.[17] However, several attempts to perform this conversion were not met with success. This may be due to the fact that the essential intermediate, formed by ligand exchange on titanium with ethenylcyclopropane, has a cyclopropylcarbinyltitanium substructure and as such would be prone to undergo a rapid rearrangement of the type (cyclopropylcarbinyl)metal to (homoallyl)metal.[18] The resulting titanacyclohex-3-ene might not be reactive enough to undergo insertion of the dibenzylformamide, but simply be hydrolyzed upon aqueous work-up to yield pent-2-ene, which would have been lost due to its volatility. In order to access 2-cyclopropylcyclopropanamine (**13**), ethyl 2-cyclopropylcyclopropanecarboxylate (**9**) was prepared in 80% yield by rhodium(II)-catalyzed cyclopropanation of **5** with ethyl diazoacetate (Scheme 3).

Alternatively, **9** was prepared in 79% overall yield by sequential cyclopropanation of buta-1,3-diene (**10**) with ethyl diazoacetate under dirhodium tetraacetate catalysis[19] and diiodomethane/diethylzinc/trifluoroacetic acid.[20] Curtius degradation of 2-cyclopropylcyclopropanecarboxylic acid (**11**), obtained upon hydrolysis of the ester **9**, employing the Weinstock protocol[21] just like in the synthesis of 1-cyclopropylcyclopropanamine,[1] furnished the *N*-Boc-protected 2-cyclopropylcyclopropanamine **12**. Deprotection of **12** with hydrogen chloride in diethyl ether and subsequent treatment with sodium hydroxide gave pure (after distillation) 2-cyclopropylcyclopropanamine (**13**) in an overall yield of 55% (from **11**).

^{1}H and ^{13}C NMR spectra were recorded at 300 MHz (^{1}H) or 75.5 MHz (^{13}C, additional DEPT) on a Varian Mercury VX300 instrument in $CDCl_3$ solutions, $CHCl_3$/$CDCl_3$ as internal references. IR spectra were obtained with a Bruker Alpha FT-IR instrument. EI-MS, ESI-MS, and HRMS spectra were measured with Finnigan MAT 95 (at 70 eV), Finnigan LCQ, and Bruker Daltonic APEX IV 7T FTICR instruments, respectively. Elemental analyses were performed in St. Petersburg with a Hewlett-Packard CHN-Analyzer HP 185B. TLC analyses were performed on precoated sheets (0.25 mm Sil G/UV254) from Macherey-Nagel. All chemicals were used as commercially available. Anhyd Et_2O was obtained by distillation from sodium benzophenone ketyl, acetone by distillation from anhyd K_2CO_3, and pyridine by distillation from CaH_2. Organic ex-



Scheme 3 Preparation of 2-cyclopropylcyclopropanamine (**13**)

tracts were dried over $MgSO_4$, if not otherwise specified. All reactions in anhyd solvents were carried out under an argon atmosphere in flame-dried glassware.

Bromomethyl Cyclopropyl Ketone (2)[10]

To a solution of cyclopropyl methyl ketone (**1**, 52.4 g, 0.623 mol) in MeOH (370 mL), kept at 0–10 °C, was added with continuous stirring Br_2 (99.6 g, 31.9 mL, 0.623 mol) within 1 h. The reaction was autocatalytic and proceeded slowly at the beginning. The resulting colorless solution was stirred at 0–10 °C for an additional 30 min, before H_2O (190 mL) was added, and the mixture stirred for an additional 15 min. Then H_2O (1 L) was added and the mixture extracted with CH_2Cl_2 (4 × 100 mL). The combined organic phases were washed with 2 M Na_2CO_3 solution, H_2O, and brine, dried ($MgSO_4$), and cautiously concentrated (30 °C/100–200 Torr). As **2** is extremely lachrymatory, it was used without further purification.

2-Bromo-1-cyclopropylethanol (3)[10]

To a solution of crude **2** [from **1** (52.4 g)] in MeOH (350 mL) was added with stirring at 0 °C $NaBH_4$ (5.9 g, 0.16 mol) in several portions within 20 min, and the resulting clear solution was stirred at 0 °C for an additional 20 min, then diluted with H_2O (500 mL) and extracted with CH_2Cl_2 (4 × 50 mL). The combined organic phases were washed with half-concentrated NaCl solution, dried ($MgSO_4$), and carefully concentrated (40 °C/100–200 Torr). The bromohydrin **3** can be distilled under reduced pressure (bp 88–95 °C/13–18 Torr), but this is not necessary for the next step; yield: 82.5 g (80% over two steps).

2-Bromo-1-cyclopropylethyl Acetate (4)

To a solution of crude bromohydrin **3** (82.5 g) in anhyd pyridine (120 mL) was added, with stirring and cooling in a water bath, Ac_2O (71 g, 0.70 mol) within 1 h. The resulting solution was left standing overnight, then a mixture of H_2O (400 mL) and ice (100 g) was added. The mixture was extracted with Et_2O (300 mL), the organic phase was washed with 2 M HCl, H_2O, and brine, dried ($MgSO_4$), and cautiously concentrated (40 °C/100–200 Torr). The residue was distilled under reduced pressure (bp 90–92 °C/10 Torr) to give **4** (93.7 g, 91%).

IR (neat): 3087, 3012, 1733, 1369, 1223, 1017, 978 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 0.35 (m, 1 H), 0.48 (m, 1 H), 0.59 (m, 2 H), 1.11 (m, 1 H), 2.10 (s, 3 H), 3.51 (dd, *J* = 10.8, 6.4 Hz, 1 H), 3.59 (dd, *J* = 10.8, 4.0 Hz, 1 H), 4.41 (m, 1 H).

^{13}C NMR/APT (75.5 MHz, $CDCl_3$): δ = 3.0 (CH_2), 3.4 (CH_2), 13.8 (CH), 20.9 (CH_3), 34.1 (CH_2), 76.6 (CH).

HRMS (ESI$^+$): *m*/*z* [M + Na]$^+$ calcd for $C_7H_{11}BrNaO_2$: 230.9820/228.9840; found: 230.9814/228.9835.

Anal. Calcd for $C_7H_{11}BrO_2$: C, 40.60; H, 5.35. Found: C, 40.45; H, 5.45.

Ethenylcyclopropane (5)

A mixture of bromohydrin acetate **4** (82.5 g, 0.432 mol), AcONa (37 g, 0.45 mol), and Zn/Cu couple (75 g, prepared from zinc dust according to the established protocol[19]) in glacial AcOH (550 mL) was slowly heated with stirring to 110–120 °C (bath temperature), during which time the formed ethenylcyclopropane (**5**) was distilled off through a 30-cm Vigreux column into a receiving flask cooled with dry ice/acetone. The vigorous phase of the reaction lasted for about 20 min, and within another 30 min the distillation of the product was complete (bp 40–70 °C). The distillate was washed with H_2O, dried ($MgSO_4$), and distilled once more over a 30-cm Vigreux column (bp 40–41 °C) to give **5** (20.9 g, 77%). The spectroscopic data were as published before.[6f]

1-Bromo-2-cyclopropylcyclopropane (*cis*/*trans*-7)

Method a: To a solution of 2,2-dibromobicyclopropyl[4c] (**6**, 32.0 g, 0.133 mol) and Ti(O*i*-Pr)$_4$ (2.0 mL, 6.7 mmol) in anhyd Et_2O (22 mL) was added, with continuous stirring and cooling in a water bath under an atmosphere of N_2, 0.95 M EtMgBr in Et_2O (245 mL, 0.23 mol) within 45 min. The mixture was stirred for an additional 10 min, before H_2O (54 mL), then 15% H_2SO_4 (220 mL), were added cautiously. The aqueous phase was extracted with pentane (2 × 70 mL), the combined organic phases were washed with H_2O and brine, and then dried ($MgSO_4$). The solvents were slowly distilled off through a 30-cm Vigreux column with a distillation head, and the residue was distilled through the same column under reduced pressure (bp 69–72 °C/48 Torr). For the final purification the product was diluted with pentane (10 mL) and subjected to flash column chromatography (silica gel, 120 mL, pentane). The resulting solution was carefully concentrated on a rotatory evaporator at 25–30 °C bath temperature. The residue was pure **7** (9.7 g, 45%); ratio *cis*/*trans* 45:55.

^1H NMR (300 MHz, $CDCl_3$): δ = 0.0–0.9 (m, 7 H), 1.08 (m, 0.55 H), 1.32 (m, 0.45 H), 2.60 (m, 0.45 H), 3.03 (m, 0.55 H).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 2.3 (CH_2), 3.2 (CH_2), 3.9* (CH_2), 4.2* (CH_2), 11.0 (CH), 11.4* (CH), 13.7 (CH_2), 13.8* (CH_2), 18.6 (CH), 20.5* (CH), 23.3*(CH), 24.5 (CH). * Refers to major diastereomer.

^1H NMR (300 MHz, $CDCl_3$), IR, MS, as well as elemental analysis data have been reported before.[8a]

Method b: To 2,2-dibromobicyclopropyl[4c] (**6**, 78.0 g, 0.325 mol) warmed at 30 °C was added dropwise *n*-Bu_3SnH (94.5 g, 0.325 mol) at such rate that the internal temperature did not exceed 45 °C (exothermic reaction). The mixture was stirred at 35–40 °C for an additional 1 h, the product was distilled twice under reduced pressure to yield *cis*/*trans*-**7** (39.0 g, 75%); bp 78 °C/70 Torr.

2-(Bicyclopropyl-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (8)

To a solution of 1-bromo-2-cyclopropylcyclopropane (*cis*/*trans*-**7**, 1.66 g, 10.3 mmol) in anhyd Et_2O (35 mL), kept at dry ice/acetone temperature, was added, with stirring under an atmosphere of N_2, 1.2 M *t*-BuLi in pentane (10 mL) within 15 min, and the mixture was stirred at the same temperature for an additional 30 min. From a syringe, 2-isopropoxy-1,3,2-dioxaborolane (1.92 g, 10.3 mmol) was added within 10 min, and the mixture was stirred at dry ice temperature for 3 h, then the mixture was warmed up to r.t. and the reaction quenched by addition of sat. NH_4Cl solution (10 mL). The aqueous phase was extracted with Et_2O (3 × 10 mL), the combined organic phases were washed with brine, dried ($MgSO_4$), and concentrated under reduced pressure on a rotatory evaporator. The residue was taken up in Et_2O–pentane (1:10, 2 mL) and subjected to flash column chromatography (R_f = 0.5) to yield *cis*/*trans*-**8** (2.06 g, 96%); ratio 1:1.

IR (neat): 3076, 2978, 1409, 1315, 1214, 1143, 858 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = –0.40 to 0.80 (m, 9 H), 1.20 (s, 6 H), 1.22 (s, 3 H), 1.25 (s, 3 H).

^{13}C NMR/APT (75.5 MHz, $CDCl_3$): δ = –2 (br, CH), 2.6 (CH_2), 3.2 (CH_2), 4.6 (CH_2), 4.9 (CH_2), 9.2 (CH_2), 9.9 (CH_2), 11.7 (CH), 13.0 (CH), 19.9 (CH), 21.8 (CH), 24.5 (CH_3), 24.6 (CH_3), 24.7 (CH_3), 25.1 (CH_3), 82.8 (C).

MS (EI): *m*/*z* = 207 (M$^+$), 193, 179, 165, 151, 123, 107, 84, 67, 55.

Ethyl 2-Cyclopropylcyclopropanecarboxylate (*cis*/*trans*-9) from Ethenylcyclopropane (5)

A solution of ethyl diazoacetate (10.0 g, 88.1 mmol) in CH_2Cl_2 (30 mL) was added dropwise (syringe pump) to a stirred solution of ethenylcyclopropane (**5**, 5.00 g, 73.4 mmol) and $[Rh(OAc)_2]_2$ (0.15

g) in CH_2Cl_2 (30 mL) at 0 °C within 6 h. After 2 h of additional stirring, the solvent was removed by distillation, and the product was isolated by column chromatography (silica gel, pentane–Et_2O, 20:1). After removal of the solvent, the residue was distilled in vacuo to give *cis*/*trans*-**9** (9.08 g, 80%) as a colorless liquid; ratio *cis*/*trans* ca. 1:1.4; bp 74–76 °C/8 Torr.

IR (thin film): 3081 (cPr–H), 1721 cm^{-1} (C=O).

^1H NMR (300 MHz, $CDCl_3$): δ = 0.05–0.20 (m, 1.2 H, cPr-H), 0.25–0.56 (m, 2 H, cPr-H), 0.64–0.70 (m, 0.5 H, cPr-H), 0.96–1.14 (m, 1.2 H, cPr-H), 1.22–1.31 (m, 2.6 H, CH_3, cPr-H), 1.36–1.47 (m, 1 H, cPr-H), 1.62–1.71 (m, 0.5 H, cPr-H), 4.06–4.19 (m, 4 H, CH_2O).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 2.5/3.6 (CH_2), 4.4/4.9 (CH_2), 8.6/11.5 (CH), 13.0/13.2 (CH_2), 14.2/14.3 (CH_3), 19.1/19.2 (CH), 24.6/25.7 (CH), 60.2/60.3 (CH_2), 172.8/174.3 (C=O).

MS (EI): *m*/*z* = 154 (M^+), 125, 109, 97, 81, 79, 54.

Ethyl 2-Cyclopropylcyclopropanecarboxylate (*cis*/*trans*-9) from Buta-1,3-diene

Ethyl 2-Ethenylcyclopropanecarboxylate

Ethyl diazoacetate (67 g, 0.587 mol) was added dropwise (30 min) to a solution of buta-1,3-diene (**10**, 259 mL, 165 g, 3.07 mol) and $[Rh(OAc)_2]_2$ (0.95 g) in CH_2Cl_2 (260 mL) at –3 to –5 °C for 4.5 h. After 1 h at this temperature, the excess buta-1,3-diene was allowed to evaporate. The solvent was removed on a rotatory evaporator, and the product was isolated by distillation to give ethyl 2-ethenylcyclopropanecarboxylate (73.0 g, 88%) as a colorless liquid; ratio *cis*/*trans* ca. 1:1.2; bp. 55–65 °C/8 Torr.

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0/15.4 (CH_2), 14.2/14.3 (CH_3), 20.9/21.8 (CH), 24.7/25.4 (CH), 60.4/60.5 (CH_2), 114.7/116.0 (=CH_2), 135.3/138.0 (=CH), 171.9/173.3 (C=O).

^1H NMR, IR, MS spectra were published previously along with the CuCl-catalyzed cyclopropanation of buta-1,3-diene with ethyl diazoacetate, which gave the title compound in only 27% yield.[8a]

Ethyl 2-Cyclopropylcyclopropanecarboxylate (*cis*/*trans*-9)

Et_2Zn (79.8 g, 66 mL, 646 mmol) was added to anhyd CH_2Cl_2 (1.5 L) at 0 °C in an inert atmosphere, and then to this solution was added TFA (73.7 g, 49.5 mL, 646 mmol) dropwise at 0 °C over a period of 2 h. To the solution was added CH_2I_2 (173 g, 52.0 mL, 646 mmol) dropwise over a period of 15 min. The resulting solution was stirred at 0 °C for 30 min, at which time ethyl 2-ethenylcyclopropanecarboxylate (41.17 g, 294 mmol) was added. The mixture was stirred at 0 °C for 30 min and then at r.t. for 16 h. The reaction was quenched by addition of sat. aq NH_4Cl (600 mL). The organic layer was separated and washed with H_2O (300 mL), dried, and filtered, and the solvent was removed on a rotatory evaporator. The resulting liquid was distilled under reduced pressure. The fraction boiling at 69–73 °C/7 Torr was collected to give *cis*/*trans*-**9** (40.8 g, 90%) as a colorless liquid; ratio *cis*/*trans* ca. 1:1.2.

2-Cyclopropylcyclopropanecarboxylic Acid (*cis*/*trans*-11)

A solution of KOH (27.0 g, 0.481 mol) in H_2O (80 mL) was slowly added to a stirred solution of the ester *cis*/*trans*-**9** (49.6 g, 0.322 mol) in MeOH (270 mL) and the mixture was stirred at r.t. for 15 h. The mixture was concentrated on a rotatory evaporator, and the residue was acidified with HCl to pH 2–3. The product was extracted with Et_2O, and the extract was washed with brine and dried. The solvent was removed on a rotatory evaporator to give the practically pure acid *cis*/*trans*-**11** (39.1 g, 95%; *cis*/*trans* ca. 1:1.2), which was used without further purification.

^1H NMR (300 MHz, $CDCl_3$): δ = 0.06–0.59 (m, cPr-H), 0.74–0.93 (m, cPr-H), 1.05–1.19 (m, cPr-H), 1.38–1.44 (m, cPr-H), 1.48–1.56 (m, cPr-H), 1.66–1.73 (m, cPr-H), 11.73 (br s, OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 2.6/3.7 (CH_2), 4.5/5.0 (CH_2), 8.5/11.5 (CH), 14.1/14.2 (CH_2), 19.0/19.2 (CH), 25.9/27.1 (CH), 179.8/181.0 (C=O).

***tert*-Butyl *N*-(2-Cyclopropylcyclopropyl)carbamate (*cis*/*trans*-12)**

To a mechanically stirred solution of the acid *cis*/*trans*-**11** (39.1 g, ca. 310 mmol) in anhyd acetone (940 mL), was added Et_3N (42.2 g, 58.1 mL, 417 mmol) dropwise at –5 °C. After additional stirring at this temperature for 15 min, neat ethyl chloroformate (57.4 g, 50.4 mL, 529 mmol) was added at the same temperature over a period of 30 min, and the resulting mixture was stirred at this temperature for an additional 2 h. Then a solution of NaN_3 (41.5 g, 0.554 mmol) in H_2O (110 mL) was added over a period of 1 h. The mixture was stirred at 0 °C for 1.5 h, concentrated under reduced pressure at 0 °C to about half of the original volume, poured into ice-cold H_2O (1.1 L), and the mixture extracted with Et_2O (4 × 200 mL) and pentane (2 × 180 mL). The combined organic solutions were washed with ice-cold H_2O (2 × 200 mL), dried (under stirring with $MgSO_4$, 0 °C, 1 h) and concentrated under reduced pressure (0 °C/20–30 Torr). The residue was taken up with pentane (200 mL), dried, and concentrated under the same conditions. It was then dissolved in anhyd *t*-BuOH (110 mL), and this solution was added dropwise to anhyd *t*-BuOH (720 mL) kept at 80 °C under vigorous stirring over a period of 2.5 h. The resulting solution was heated under reflux for an additional 9 h. The main volume of *t*-BuOH (ca. 700 mL) was distilled off at ambient pressure under a flow of N_2. After cooling, the residue was dried (20 °C/0.1 Torr) to give essentially pure carbamate *cis*/*trans*-**12** (51.0 g, 83%) as a viscous oil, which was used in the next step without further purification.

^1H NMR (300 MHz, $CDCl_3$): δ = 4.71/4.64 (br s, NH), 2.59/2.25 (br s, *c*Pr-H), 1.45/1.44 (s, CH_3), 1.28–1.22 (br m, *c*Pr-H), 1.02–0.93 (br m, *c*Pr-H), 0.92–0.83 (br m, *c*Pr-H), 0.82–0.72 (br m, *c*Pr-H), 0.66–0.57 (br m, *c*Pr-H), 0.57–0.43 (m, *c*Pr-H), 0.41–0.30 (m, *c*Pr-H), 0.23–0.15 (m, *c*Pr-H), 0.12–0.04 (m, *c*Pr-H).

2-Cyclopropylcyclopropan-1-amine (*cis*/*trans*-13)

Under stirring, a solution of *cis*/*trans*-**12** (51.0 g, 259 mmol) in Et_2O (60 mL) was added to a ca. 5.0 N HCl solution in Et_2O (400 mL) in one portion at 0 °C. The mixture was stirred at 0 °C for 4 h and at r.t. for 20 h. The solvent was removed on a rotatory evaporator, and the residue was dissolved in H_2O (300 mL), the solution was washed with Et_2O (2 × 70 mL), and the aq solution of the hydrochloride was alkalified with 30% aq NaOH to pH 10–11 under cooling. The amine was extracted with Et_2O (6 × 100 mL), the extract was dried (Na_2SO_4), and the solvent was removed by distillation through a 30-cm Vigreux column. The product was purified by distillation (bp 63–65 °C/65 Torr) to give *cis*/*trans*-**13** (17.66 g, 70%) as a colorless liquid; ratio *cis*/*trans* ca. 1:1.2.

^1H NMR (300 MHz, $CDCl_3$): δ = 2.33–2.27 (m, *c*Pr-H), 2.07–2.03 (m, *c*Pr-H), 1.49 (br s, NH), 0.78–0.68 (m, *c*Pr-H), 0.62–0.42 (m, *c*Pr-H), 0.38–0.14 (m, *c*Pr-H), 0.07–0.04 (m, *c*Pr-H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 2.6/3.2 (CH_2), 3.9/4.1 (CH_2), 7.6/11.0 (CH), 12.5/12.7 (CH_2), 20.9/23.3 (CH), 28.6/29.6 (CH).

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