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Supporting Information

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Helicity of [1,1';1',1'';…;1^{n-2},1^{n-1}]Oligocyclopropanes: Synthesis and Structure of a [1,1';1',1'';1'',1''';1''',1'''']Quinquecyclopropane**

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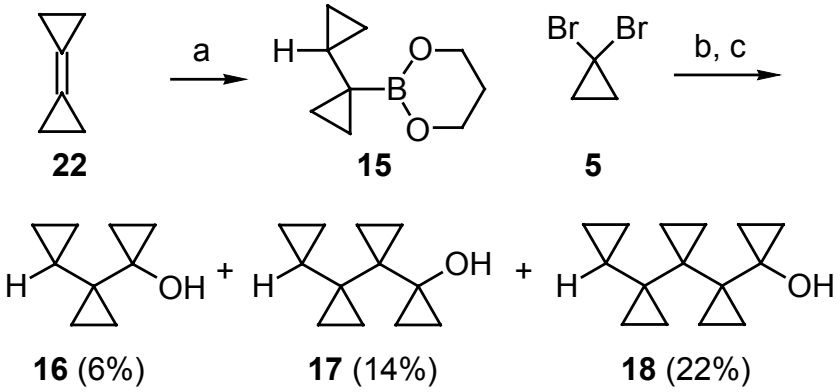
In order to obtain even higher 1,1-linked oligocyclopropane derivatives of this type, the Matteson homologation was also applied towards 2-(bicyclopropyl-1-yl)-[1,3,2]dioxaborinane (**15**). The latter was prepared adopting a published protocol[1] and used on bicyclopropylidene (**22**);[2] however, the yield was only 27% (Scheme 1).



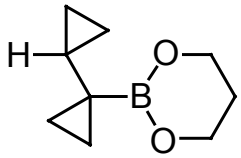
Scheme 1. Synthesis of 2-(bicyclopropyl-1-yl)-[1,3,2]dioxaborinane (**15**) and oligocyclopropylcyclopropanols **16**–**18**. Reagents and conditions: a) BH_3·THF, THF, 0–20 °C, 5 h, then $HO(CH_2)_3OH$, THF, 20 °C, 14 h; b) *n*BuLi, THF, –110 °C, 20 min, then **15**, –110 °C, 1.3 h, –110 to 20 °C, 12 h; c) **5**, then *n*BuLi, –110 °C, 1.3 h, –110 to 20 °C, 12 h; this procedure was repeated three more times.

However, application of the described above protocol for the homologation with the bromolithium carbenoid from **5** as towards the borinate **15** gave essentially the same results: only the diols **16**–**18** were isolated from the reaction mixture and these even in lower yields (Scheme 1).

Experimental Section

General aspects: Bicyclopropylidene (**22**)[3] and 1,1-dibromocyclopropane (**5**)[4] were prepared according to previously published procedures. 2-Cyclopropyl[1,3,2]dioxaborinane

(**14**) was synthesized by cyclopropanation of the known 2-vinyl[1,3,2]dioxaborinane[5a] adopting a previously published procedure.[5b,c] All operations in anhydrous solvents were performed under argon in flame-dried glassware. THF was dried by distillation from sodium benzophenone ketyl. All other chemicals were used as commercially available. Organic extracts were dried over $MgSO_4$. TLC analyses were performed on precoated sheets, 0.25 mm Sil G/UV_{254} (Macherey-Nagel). Silica gel grade 60 (230–400 mesh) (Merck) was used for column chromatography. NMR spectra of solutions in $CDCl_3$ were recorded on a Bruker AM 250 (250 MHz for ^1H and 62.9 MHz for ^{13}C NMR) instrument. Multiplicities were determined by DEPT (Distortionless Enhancement by Polarization Transfer) measurements. Chemical shifts refer to $\delta_{TMS} = 0.00$ according to the chemical shifts of residual $CHCl_3$ signals.

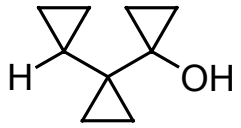


15

2-(Bicyclopropyl-1-yl)-[1,3,2]dioxaborinane (15): To a vigorously stirred solution of borane in THF (60 mL of a 1 M solution) was added dropwise a solution of bicyclopropylidene (**22**) (2.80 g, 3.28 mL, 35.0 mmol) in anhydrous THF (8 mL) at 0 °C over a period of 2 h. The resulting solution was stirred for an additional 1 h at this temp. and then for 2 h at ambient temp. This solution was taken up with a syringe and added dropwise at ambient temp. over a period of 2 h to a second flask which contained 30 mL of anhydrous THF, and 1,3-propandiol (8.42 g, 8.0 mL, 111 mmol) was added simultaneously.[6] The reaction mixture was stirred at this temp. overnight, then concentrated under reduced pressure, and the residue was "bulb-to-bulb" distilled to a cold trap (vacuum 0.1 Torr, bath temperature 75 °C). The distillate was taken up with diethyl ether (50 mL), the solution washed with ice-cold water and brine (20 mL each), dried and concentrated under reduced pressure again. Distillation of the residue under reduced pressure furnished the borinane **15** (1.57 g, 27%) as a colorless liquid, bp 64 °C (4 mbar). ^1H NMR (250 MHz, $CDCl_3$): $\delta = 3.97$ (t, $J = 5.5$ Hz, 4 H; 2 OCH_2), 1.95 (p, $J = 5.5$ Hz, 2 H; CH_2), 1.10 (m, 1 H; *c*Pr-H), 0.42 (dd, $J = 3.2, 5.8$ Hz, 2 H; *c*Pr-H), 0.26–0.18 (m, 2 H; *c*Pr-H), 0.09 (dd, $J = 3.0, 5.5$ Hz, 2 H; *c*Pr-H), –0.13 (dt, $J = 4.0, 5.5, 5.8$ Hz, 2 H; *c*Pr-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 61.7$ (2 CH_2), 27.3 (CH_2), 12.3 (CH), 7.9 (2 CH_2), 5.0 (C, br.), 1.4 (2 CH_2).

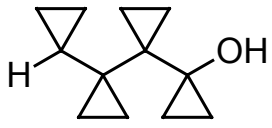
[1,1';1',1'']Tercyclopropan-1-ol (16), [1,1';1',1'';1'',1''']Quatercyclopropan-1-ol (17) and [1,1';1',1'';1'',1''';1''',1'''']Quinquecyclopropan-1-ol (18): To a stirred solution of 1,1-dibromocyclopropane **5** (2.00 g, 10.0 mmol) in anhydrous THF (50 mL) was added dropwise

n-butyllithium (10.0 mmol, 3.85 mL of a 2.60 M solution in hexane) at –110 °C over a period of 15 min. After stirring for an additional 5 min at this temp., a solution of the borinate **15** (1.50 g, 9.00 mmol) in THF (8 mL) was added dropwise at the same temp. over a period of 20 min and, after stirring at this temp. for an additional 1 h, the reaction mixture was allowed to warm up to ambient temp. over a period of 12 h. Dibromocyclopropane **5** (2.00 g, 10.0 mmol) was added, the mixture was cooled to –110 °C and treated with *n*-butyllithium (10.0 mmol, 3.85 mL of a 2.60 M solution in hexane) again as described above, then the reaction mixture was allowed to warm up again to ambient temp. over a period of 12 h. This operation was repeated three more times, then the reaction mixture was treated with hydrogen peroxide (4.54 g, 4.10 mL of a 30% aq. solution, 40.0 mmol) and sodium hydroxide (25 mL of a 1 N aq. solution, 25.0 mmol) at 0 °C, and the resulting mixture stirred unter argon at 25 °C for 6 h. The mixture was extracted with diethyl ether (6 × 70 mL), the combined organic extracts were dried and concentrated under reduced pressure at 0 °C bath temperature.[7] Column chromatography of the residue (2.19 g) on silica gel (350 g of silica gel, 5 × 40 cm column, hexane/Et_2O 10:1 to 4:1) furnished [1,1';1',1";1",1'";1'",1'"']quinquecyclopropan-1-ol (**18**) (437 mg, 22%, R_f = 0.25 in hexane/Et_2O 4:1), [1,1';1',1";1",1'"]quatercyclopropan-1-ol (**17**) (233 mg, 14.4%, R_f = 0.20 in hexane/Et_2O 4:1) and [1,1';1',1"]tercyclopropan-1-ol (**16**) (76 mg, 6.1%, R_f = 0.15 in hexane/Et_2O 4:1) as colorless oils.



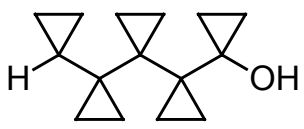
16

[1,1';1',1"]Tercyclopropan-1-ol (16): ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.38 (br, 1 H; OH), 1.40–1.25 (m, 1 H; CH), 0.68–0.60 (m, 2 H; CH_2), 0.49–0.33 (m, 4 H; CH_2), 0.12–0.27 (m, 4 H; CH_2), 0.09 to –0.04 (m, 2 H; CH_2); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 60.58 (C-OH), 24.65 (C), 13.26 (CH), 11.63 (2 CH_2), 7.67 (2 CH_2), 1.45 (2 CH_2).



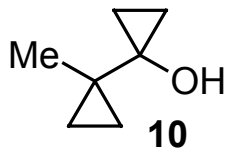
17

[1,1';1',1";1",1'"]Quatercyclopropan-1-ol (17): ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.43 (br, 1 H; OH), 1.48–1.36 (m, 1 H; CH), 0.70 (dd, *J* = 5.0, 7.3 Hz, 2 H; CH_2), 0.50 (dd, *J* = 4.8, 7.0 Hz, 2 H; CH_2), 0.43–0.38 (m, 2 H; CH_2), 0.32–0.28 (m, 4 H; CH_2), 0.22–0.13 (m, 4 H; CH_2), 0.07–0.01 (m, 2 H; CH_2); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 59.6 (C-OH), 27.5 (C), 22.5 (C), 15.2 (CH), 12.1 (2 CH_2), 8.6 (2 CH_2), 6.4 (2 CH_2), 2.4 (2 CH_2).



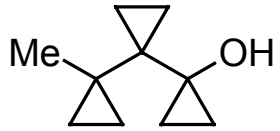
18

[1,1';1',1'';1'',1''';1''',1'''']Quinquecyclopropan-1-ol (18): ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.55 (br, 1 H; OH), 1.66–1.57 (m, 1 H; CH), 0.71–0.66 (m, 2 H; CH_2), 0.56–0.51 (m, 2 H; CH_2), 0.49–0.44 (m, 2 H; CH_2), 0.39–0.31 (m, 2 H; CH_2), 0.29–0.21 (m, 6 H), 0.12–0.06 (m, 4 H; CH_2), –0.02 to –0.09 (m, 2 H; CH_2); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 59.9 (C-OH), 25.7 (C), 25.2 (C), 23.6 (C), 14.8 (CH), 12.4 (2 CH_2), 9.7 (2 CH_2), 8.0 (2 CH_2), 7.5 (2 CH_2), 1.9 (2 CH_2). The structure of **18** was proved by X-ray crystal structure analysis of its 3,5-dinitrobenzoate (**18**-DNB).[8]



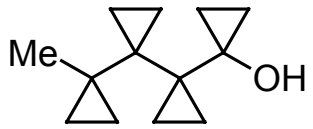
10

^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.22 (br, 1 H; OH), 1.20 (s, 3 H; CH), 0.62 (m, 2 H; CH_2), 0.42–0.23 (m, 6 H; CH_2); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 60.51 (C-OH), 21.26 (CH_3), 20.08 (C), 11.91 (2 CH_2), 11.51 (2 CH_2).



11

^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.24 (br, 1 H; OH), 1.23 (s, 3 H; CH_3), 062 (m, 2 H; CH_2), 0.39 (m, 2 H; CH_2), 0.33–0.19 (m, 8 H; CH_2); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 59.60 (C-OH), 27.09 (C), 23.54 (CH_3), 17.88 (C), 11.74 (2 CH_2), 10.55 (2 CH_2), 8.56 (2 CH_2).

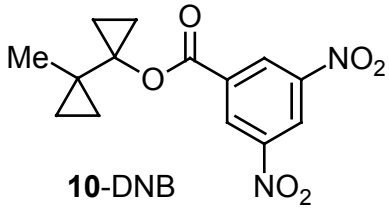


12

^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.39 (br, 1 H; OH), 1.19 (s, 3 H; CH), 0.67 (m, 2 H; CH_2), 0.52 (m, 2 H; CH_2), 0.43 (m, 2 H; CH_2), 0.32–0.28 (m, 4 H; CH_2), 0.27–0.16 (m, 6 H; CH_2); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 59.88 (C-OH), 25.35 (C), 24.79 (C), 24.11 (C H_3), 19.52 (C), 12.45 (2 CH_2), 11.80 (2 CH_2), 9.28 (2 CH_2), 8.16 (2 CH_2).

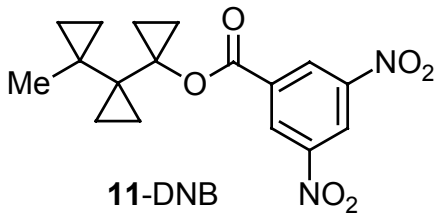
Preparation of 3,5-dinitrobenzoates of [1,1';1',1'';…;1^{n-2},1^{n-1}]oligocyclopropanols 10-DNB, 11-DNB, 12-DNB and 18-DNB. General procedure (GP) 1

A mixture of the respective oligocyclopropanol (0.23 mmol), 3,5-dinitrobenzoyl chloride (DNBC, 0.25 mmol), and DMAP (8 mg) in pyridine (3 mL) was stirred at 40 °C for 30 h under argon. The reaction mixture was diluted with diethyl ether (100 mL) and washed with saturated aqueous copper(II) sulfate (5 × 20 mL) to remove pyridine. The organic layer was dried, the solvent was evaporated under reduced pressure, and the residue was purified by column chromatography. The structure of the product was proved by X-ray crystal structure analysis.[8]



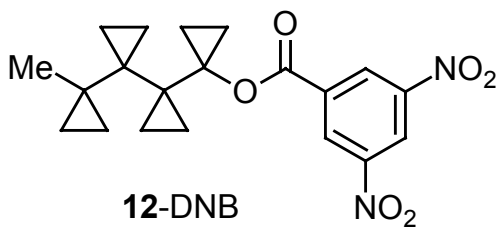
10-DNB

1'-Methylbicyclopropyl-1-yl 3,5-dinitrobenzoate (10-DNB): Column chromatography (25 g of flash silica gel, 2 × 40 cm column, hexane/ether = 4:1, R_f = 0.35) of the crude product obtained from the alcohol **10** (30 mg, 0.27 mmol) and DNBC (67 mg, 0.29 mmol) according to GP1 furnished **10**-DNB (67 mg, 81%) as a yellow oil which could be crystallized from hexane to give pale yellow plate-like crystals; mp 122 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 9.22 (t, *J* = 2.2 Hz, 1 H; Ar-H), 9.13 (d, *J* = 2.2 Hz, 2 H; Ar-H), 1.27 (s, 3 H; CH_3), 1.07–1.00 (m, 2 H; CH_2), 0.85–0.80 (m, 2 H; CH_2), 0.67 (dd, *J* = 4.8, 6.3 Hz, 2 H; CH_2), 0.40 (dd, *J* = 4.8, 6.3 Hz, 2 H; CH_2). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 162.1 (CO), 148.6 (2 Ar-C), 134.6 (Ar-C), 129.4 (2 Ar-CH), 122.2 (Ar-CH), 67.3 (C-OR), 22.0 (C), 18.5 (CH_3), 12.6 (2 CH_2), 11.1 (2 CH_2).



11-DNB

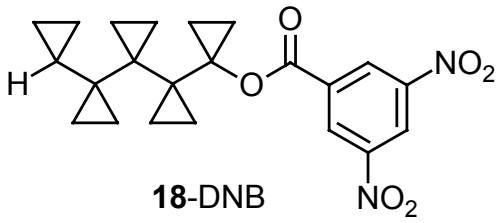
1''-Methyl-[1,1';1',1'']tercyclopropan-1-yl 3,5-dinitrobenzoate (11-DNB): **1''-Methyl-[1,1';1',1'']-tercyclopropan-1-yl 3,5-Dinitrobenzoate (11-DNB)**: Column chromatography (25 g of flash silica gel, 2 × 40 cm column, hexane/ether = 4:1, R_f = 0.42) of the crude product obtained from the alcohol **11** (30 mg, 0.20 mmol) and DNBC (69 mg, 0.30 mmol) according to GP1 furnished **11**-DNB (48 mg, 70%) as a yellow oil which could be crystallized from hexane to give pale yellow plate-like crystals; mp 109–111 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 9.23 (t, *J* = 2.2 Hz, 1 H; Ar-H), 9.14 (d, *J* = 2.2 Hz, 2 H; Ar-H), 1.37 (s, 3 H; CH_3), 1.07 (dd, *J* = 6.0, 7.5 Hz, 2 H; CH_2), 0.85–0.80 (m, 2 H; CH_2), 0.48 (dd, *J* = 6.5, 7.0 Hz, 2 H; CH_2), 0.34 (dd, *J* = 4.0, 7.3 Hz, 2 H; CH_2), 0.11–0.06 (m, 4 H; 2 CH_2); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 162.2 (CO), 148.5 (2 Ar-C), 134.7 (Ar-C), 129.4 (2 Ar-CH), 122.2 (Ar-CH), 65.6 (C-OR), 25.1 (C), 23.2 (C), 18.2 (CH_3), 11.1 (2 CH_2), 10.8 (2 CH_2), 9.4 (2 CH_2).



12-DNB

1'''-Methyl-[1,1';1',1'';1'',1''']quatercyclopropan-1-yl 3,5-dinitrobenzoate (12-DNB): Column chromatography (25 g of flash silica gel, 2 × 40 cm column, hexane/ether = 4:1, R_f = 0.44) of the crude product obtained from the alcohol **12** (31 mg, 0.16 mmol) and DNBC (69 mg, 0.30 mmol) according to GP1 furnished **12**-DNB (44 mg, 72%) as a yellow oil which could be crystallized from hexane to give pale yellow plate-like crystals; mp 104–106 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 9.22 (t, *J* = 2.0 Hz, 1 H; Ar-H), 9.10 (d, *J* = 2.0 Hz, 2 H; Ar-H), 1.19 (s, 3 H; CH_3), 1.07–1.02 (m, 2 H; CH_2), 0.96–0.90 (m, 2 H; CH_2),

0.62 (dd, J = 4.8, 6.5 Hz, 2 H; CH_2), 0.55 (m, 2 H; CH_2), 0.40 (dd, J = 4.5, 6.5 Hz, 2 H; CH_2), 0.30 (m, 2 H; CH_2), 0.11 (dd, J = 4.3, 6.3 Hz, 2 H; CH_2), –0.02 (dd, J = 3.8, 6.3 Hz, 2 H; CH_2).

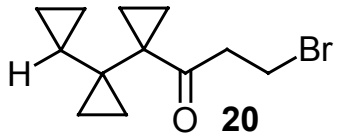


18-DNB

[1,1';1',1'';1'',1''';1''',1''''']Quinquecyclopropan-1-yl 3,5-dinitrobenzoate (12-DNB): Column chromatography (25 g of flash silica gel, 2 × 40 cm column, hexane/ether = 4:1, R_f = 0.35) of the crude product obtained from the alcohol **18** (50 mg, 0.23 mmol) and DNBC (58 mg, 0.25 mmol) according to GP1 furnished **18**-DNB (63 mg, 67%) as a pale yellow oil which could be crystallized from hexane to give colorless plate-like crystals; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 9.19 (t, J = 2.0 Hz, 1 H; Ar-H), 9.09 (t, J = 2.0 Hz, 1 H; Ar-H), 1.52 (m, 1 H; CH), 1.00 (m, 4 H; CH_2), 0.58 (m, 4 H; CH_2), 0.21 (m, 4 H; CH_2), 0.02 (m, 6 H; CH_2), 0.00 (m, 2 H; CH_2); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 162.2 (CO), 148.2 (2 Ar-C), 134.7 (Ar-C), 129.3 (2 Ar-CH), 122.2 (Ar-CH), 66.2 (C-OR), 25.1 (C), 23.6 (C), 23.2 (C), 15.1 (CH), 11.6 (2 CH_2), 10.0 (2 CH_2), 7.9 (2 CH_2), 7.7 (2 CH_2), 2.1 (2 CH_2).

Preparation of 3-bromopropionyl-1,1-oligocyclopropyls 20 and 21. General procedure (GP) 2.

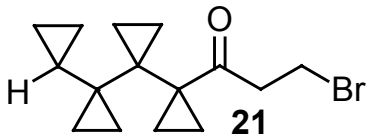
To a stirred solution of triphenylphosphane (1.05 equiv.) in anhydrous dichloromethane (10 mL), was added bromine (1.05 equiv.) as a solution in CH_2Cl_2 (5 mL) at –30 to –15 °C over a period of 5 min. After an additional 15 min of stirring, the mixture was cooled to –78 °C, and a solution of the respective alcohol (1.00 equiv) and anhydrous pyridine (1.00 equiv.) in CH_2Cl_2 (3 mL) was added dropwise. The resulting mixture was allowed to warm up to ambient temperature within 20 h and then concentrated under reduced pressure. Pentane (20 mL) was added, the mixture was stirred at ambient temp. for 3 h and then filtered. The precipitate was thoroughly washed with pentane (3 × 10 mL), the combined pentane extracts were filtered through a 0.5-cm pad of silica gel. After concentration of the filtrate under reduced pressure, the product was purified by column chromatography.



20

(3-Bromo-1-[1,1';1',1'']tercyclopropan-1-yl)propan-1-one (20): Column chromatography (40 g of silica gel, 2 × 30 cm

column, hexane/ether = 6:1, R_f = 0.45) of the crude product obtained from the alcohol **17** (230 mg, 1.29 mmol), Ph_3P (355 mg, 1.36 mmol), Br_2 (216 mg, 69 μL, 1.36mmol) and pyridine (102 mg, 104 μL, 1.29 mmol), according to GP2, furnished the bromoketone **20** (212 mg, 64%) as a yellow oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.61 (t, *J* = 6.9 Hz, 2 H; CH_2Br), 3.39 (t, *J* = 6.9 Hz, 2 H; CH_2), 1.23–1.18 (m, 1 H; CH), 1.13–1.07 (m, Hz, 2 H; CH_2), 0.65–0.61 (m, 2 H; CH_2), 0.39–0.31 (m, 6 H; CH_2), 0.06–0.02 (m, 2 H; CH_2); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 208.4 (C), 42.4 (CH_2), 35.6 (C), 26.3 (CH_2), 20.1 (C), 16.1 (CH), 14.2 (2 CH_2), 9.0 (2 CH_2), 2.5 (2 CH_2).

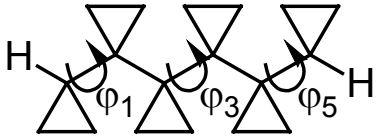


21

(3-Bromo-1-[1,1';1',1'';1'',1''']quatercyclopropan-1-yl)-propan-1-one (21): Column chromatography (40 g of silica gel, 2 × 30 cm column, hexane/ether = 6:1, R_f = 0.45) of the crude product obtained from the alcohol **18** (376 mg, 1.72 mmol), Ph_3P (474 mg, 1.81 mmol), Br_2 (289 mg, 93 μL, 1.81mmol) and pyridine (136 mg, 139 μL, 1.72 mmol), according to GP2, furnished the bromoketone **21** (471 mg, 92%) as a yellow oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.61 (t, *J* = 6.9 Hz, 2 H; CH_2Br), 3.27 (t, *J* = 6.9 Hz, 2 H; CH_2), 1.24–1.21 (m, 1 H; CH), 1.09–1.05 (m, Hz, 2 H; CH_2), 0.69–0.65 (m, 2 H; CH_2), 0.45–0.28 (m, 6 H; CH_2), 0.16–0.09 (m, 4 H; CH_2), –0.06 to –0.11 (m, 2 H; CH_2); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 207.7 (C), 42.5 (CH_2), 35.4 (C), 26.4 (CH_2), 24.2 (C), 23.9 (C), 15.1 (CH), 13.4 (2 CH_2), 8.9 (2 CH_2), 7.7 (2 CH_2), 2.4 (2 CH_2).

Geometry optimization and energies of three conformers of sexicyclopropane (19): All calculations were performed with the Gaussian 03 program package.[9] In the starting geometries all dihedral angles φ_n were set to 68° and an unrestricted geometry optimization was performed. Three different conformers were considered to asses the changes in energy associated with changing from (+)- to (–)-*gauche* orientations for single bicyclopropyl moieties (Table 1).

Table 1. Results of the geometry optimization of three different conformers of sexicyclopropane (**19**) at the B3LYP/6-31G(d) level of theory.



Cmpd.	Energy / Hartree	Rel. Energy / kcal mol^{-1}	φ_1	φ_2	φ_3	φ_4	φ_5
19a	701.366894036	±0.0	45.7	70.1	73.8	69.1	46.3
19b	701.361959246	+3.1	51.4	–49.5	85.0	–134.4	55.4
19c	701.369777306	–1.8	–55.0	60.6	62.5	59.4	–52.5

Allowing the terminal cyclopropane moieties to rotate in the direction opposite to that of the helical chain brings about a small decrease in energy of 0.9 kcal mol^{-1} per cyclopropyl moiety (**19c** vs. **19a**). However, rotation around the central bond (φ_3) gives rise to a significant increase in energy of 4.9 kcal mol^{-1} (**19c** vs. **19b**). Thus, the higher 1,1-linked oligocyclopropanes are predicted to adopt helical conformations with the exception of the terminal cyclopropane moieties to allow for minimal repulsion.

Table 2. Atomic coordinates (in Å) of the optimized structures for **19a**–**c**.

19a				H	1.909348	–1.603139	2.248514
C	2.648344	0.298203	–0.035236	C	–0.451315	0.642941	0.873241
C	2.734124	1.606174	–0.787901	C	–0.911417	1.258413	2.189655
C	3.733478	0.511964	–1.065639	C	0.162814	1.932182	1.386151
H	3.004336	0.345299	0.993534	H	–0.647610	0.808518	3.141099
H	3.060480	2.495432	–0.254612	H	–1.899598	1.710968	2.181026
H	1.989836	1.801050	–1.554926	H	–0.053406	2.880107	0.904524
H	3.666542	–0.002074	–2.021213	H	1.178189	1.859563	1.760765
H	4.753079	0.633816	–0.709345	C	–1.528224	0.699419	–0.220831
C	1.521620	–0.708088	–0.196520	C	–1.982945	2.048078	–0.762344
C	1.161025	–1.164815	–1.592188	C	–1.176596	1.121546	–1.629569
C	1.955640	–2.077886	–0.700266	H	–1.512667	2.964376	–0.420998
H	1.651049	–0.704451	–2.446981	H	–3.043737	2.151413	–0.972483
H	0.124625	–1.424754	–1.774610	H	–1.660247	0.631180	–2.471198
H	1.471317	–2.976768	–0.333138	H	–0.143506	1.390626	–1.818969
H	3.014277	–2.203689	–0.909180	C	–2.643176	–0.312971	–0.022925
C	0.450081	–0.602283	0.899462	C	–3.723515	–0.578942	–1.046268
C	–0.157421	–1.866302	1.478940	C	–2.714424	–1.651214	–0.721714
C	0.920438	–1.152107	2.241202	H	–3.002169	–0.321524	1.005974
H	0.059324	–2.835937	1.043059	H	–3.658320	–0.103748	–2.021824
H	–1.170535	–1.778416	1.856616	H	–4.743011	–0.695824	–0.688031
H	0.662145	–0.656427	3.171134	H	–3.033531	–2.520901	–0.153000

H	–1.967390	–1.870571	–1.479225

19b

C	–1.353929	1.477500	–0.278911
C	–1.619418	2.434733	0.859431
C	–2.203177	2.707179	–0.505230
H	1.777189	1.368711	–1.267563
H	–0.808153	3.061445	1.219424
H	–2.306772	2.106817	1.635293
H	–3.277896	2.609554	–0.631202
H	–1.770515	3.507470	–1.100121
C	–1.896877	0.062740	–0.295923
C	–3.395933	–0.097082	–0.147167
C	–2.753809	–0.317714	–1.492080
H	–3.996803	0.796027	–0.003293
H	–3.792612	–0.956262	0.384145
H	–2.700682	–1.339063	–1.859752
H	–2.910512	0.430591	–2.264550
C	–0.953694	–1.003354	0.292344
C	–1.206098	–1.423993	1.733721
C	–1.568892	–2.356247	0.616449
H	–2.007458	–0.919147	2.267289
H	–0.363272	–1.699798	2.360060
H	–0.956475	–3.242312	0.495280
H	–2.616555	–2.531632	0.394515
C	0.490457	–0.966689	–0.244947
C	1.107783	–2.249004	–0.789483
C	0.615267	–1.205661	–1.745482
H	0.568804	–3.188618	–0.730900
H	2.182144	–2.351330	–0.662451
H	1.343934	–0.641647	–2.316272
H	–0.305302	–1.410115	–2.282400
C	1.522704	–0.007097	0.407495
C	1.214625	0.683426	1.722622
C	2.177444	–0.471185	1.697051
H	0.244019	0.543904	2.180052
H	1.627705	1.680477	1.853616
H	3.233671	–0.278731	1.868088
H	1.844496	–1.425853	2.095583
C	2.373157	0.790103	–0.562472
C	3.672469	1.457681	–0.181811
C	3.684221	0.280540	–1.124944
H	–0.362346	1.552723	–0.715239
H	4.075298	1.313803	0.816638
H	3.865087	2.446765	–0.588981
H	3.909041	0.451061	–2.174816
H	4.066163	–0.660093	–0.736418

19c			
C	2.333796	–0.354460	–0.765347
C	3.621815	–1.106077	–1.003497
C	3.650125	0.389028	–0.796763
H	1.730753	–0.231150	–1.660851
H	3.797736	–1.494811	–2.003300
H	4.031494	–1.734015	–0.217268
H	4.046171	0.748559	0.149242
H	3.871052	1.033123	–1.644268
C	1.496549	–0.472362	0.494666
C	1.089776	–1.869911	0.920568
C	2.140718	–1.127178	1.700911
H	1.405517	–2.698616	0.292029
H	0.118521	–2.007812	1.384970
H	1.883576	–0.774647	2.694452
H	3.173421	–1.454882	1.623441
C	0.527007	0.700645	0.688278
C	0.110466	1.120006	2.088475
C	1.135162	1.928535	1.343936
H	0.422325	0.546770	2.956694
H	–0.885411	1.543876	2.181033
H	0.873584	2.926454	1.005892
H	2.170337	1.835399	1.658915
C	–0.518181	0.891004	–0.424393
C	–1.104292	2.272970	–0.656963
C	–0.086100	1.726538	–1.617830
H	–0.831927	3.108282	–0.019333
H	–2.139252	2.297853	–0.985444
H	–0.396630	1.464502	–2.624973
H	0.916694	2.140947	–1.566868
C	–1.505471	–0.267574	–0.618137
C	–2.183539	–0.456281	–1.961243
C	–1.133185	–1.435545	–1.511129
H	–1.942972	0.217413	–2.777444
H	–3.219893	–0.781634	–1.975425
H	–1.454848	–2.427308	–1.204069
H	–0.171266	–1.415726	–2.014244
C	–2.324187	–0.568756	0.623015
C	–3.653953	0.100309	0.889882
C	–3.594985	–1.384477	0.622393
H	–1.712142	–0.717281	1.508175
H	–4.064166	0.727959	0.102867
H	–3.879304	0.444456	1.896177
H	–3.751248	–2.065473	1.455194
H	–4.001235	–1.750724	–0.316534

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[6] When 1,3-propandiol was simply added to the reaction mixture, the boronate **15** was obtained in 10% yield only.

[7] Compounds **16**–**18** turned out to be highly volatile under reduced pressure.

[8] CCDC-642257 (**10**-DNB), 642256 (**11**-DNB), 642258 (**12**-DNB) and 642255 (**18**-DNB) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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