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Stereo- and regiocontrol in *ene*-dimerisation and trimerisation of 1-trimethylsilyl-3-phenylcyclopropene

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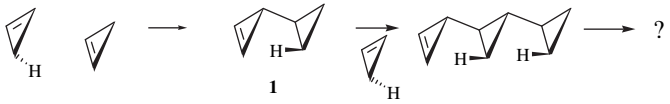
ABSTRACT

1-Trimethylsilyl-3-phenylcyclopropene and its 2D-analog undergo a highly stereocontrolled ene-reaction to give a single dimer. Further reaction leads to one or more trimers derived through two ene-reactions. The dimer formed easily undergoes cycloaddition with active dienes and nitrile oxides while the trimers do not react under the same conditions. The first enantioselective example of an ene-reaction of cyclopropene derivatives using optically active 1-trimethylsilyl-3*S*-phenylcyclopropene is also discussed.

1. Introduction

Three membered carbocycles, both saturated and unsaturated, are of interest for synthetic chemists, theoreticians and biochemists due to their unique structure resulting from the unusual geometry and high strain energy of a small ring.[1] There has been considerable recent interest in biologically active compounds containing an array of contiguous cyclopropanes.[2,3] Stereocontrolled synthesis of these compounds is usually based on the successive introduction of each small ring.[2,4] Cyclopropenes bearing a hydrogen atom at the C-3 position often undergo ene-dimerization to give cyclopropylcyclopropenes **1** (Scheme 1), which are the possible precursors of bi- and oligocyclopropanes. Formally, the further addition of starting cyclopropene molecules to the dimer **1** can lead to the formation of a single polycyclopropane. However, a high level of stereocontrol (*endo*- or *exo*-transition state) and regiocontrol during each step of the process is necessary to realize this sequence of selective transformations. In addition, such selective transformation would require the rate of reaction of the dimer **1** with cyclopropene (only one possible regio- and stereochemistry is shown) to be considerably faster than the dimerisation of these species themselves. The known examples of such reactions for substituted cyclopropenes suggest that, although the regiochemistry in dimerisations can be largely controlled by appropriate introduction of substituents, the stereochemistry (and particularly the absolute stereochemistry) is more difficult to control.[5]



Scheme 1.

It is not possible to determine the diastereoselectivity of the ene-reaction in the case of a monosubstituted cyclopropene or cyclopropene itself,[6] but asymmetrically substituted derivatives, particularly1,3-disubstituted cyclopropenes, are suitable for this purpose. Moreover, the application of enantiopure or enriched cyclopropenes in this type of reaction could be useful for the synthesis of chiral bi- and polycyclopropanes as well as providing a better understanding of the whole process.

We have recently reported the preparation and studies of the chemistry of 3-phenylcyclopropene,[7] and some of its derivatives including 1-trimethylsilyl-3-phenylcyclopropene **2** (Scheme 2).

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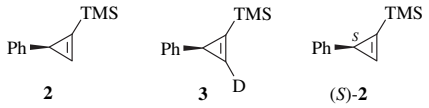
Investigation of its properties showed that under mild conditions cyclopropene **2** undergoes stereocontrolled ene-reaction giving a single dimer and two trimers in a ratio of 5:3:1, respectively. For further analysis of this ene-process, 2D-analog **3** and enriched cyclopropene (*S*)-**2** were also prepared.

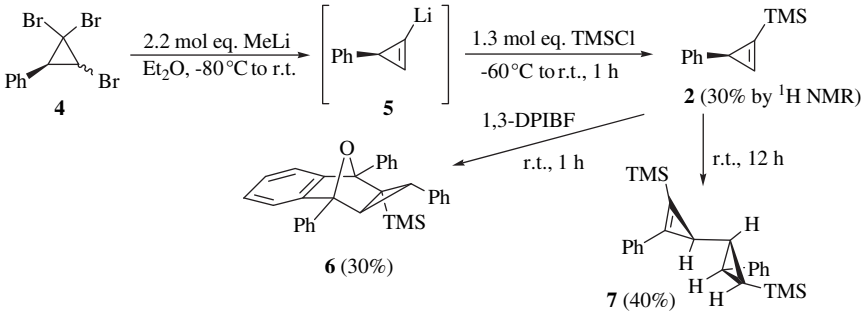


Scheme 2.

Initial results in this area (namely, generation and ene-transformations of cyclopropenes **2**, **3** and (*S*)-**2**, Scheme 2) have been represented in a short communication;[8] we now provide the details.

2. Results and discussion

Tribromocyclopropane **4** was treated with 2.2 mol equiv of MeLi at −80 °C, allowed to reach room temperature for 30 min to form the 1-lithio-3-phenylcyclopropene **5** by lithium–halogen exchange,[9] and then quenched with trimethylsilyl chloride to generate cyclopropene **2.** This could be trapped in 30% yield (from **4**) as [4+2]-cycloadduct **6** by reaction with 1,3-diphenylisobenzofuran (1,3-DPIBF).[10] In the absence of the trap, cyclopropene **2** was detected directly by ^{1}H NMR spectroscopy of the crude reaction mixture with a ca. 30% yield together with a single dimer **7**, which could be isolated in 40% yield after 12 h at room temperature (Scheme 3). The regio- and stereochemistry of **7** is established later (from now only the (*S*)-enantiomeric series is shown).



Scheme 3.

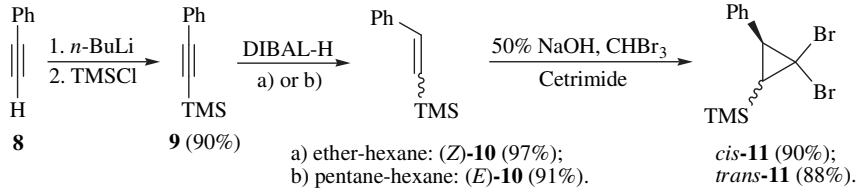
Reaction of *cis*-**11** with methyllithium was expected to lead directly to cyclopropene **2**. However, when the reaction was carried out at −90 °C and quenched with water at −50 °C, an essentially quantitative yield of allene **12** (Scheme 5) was obtained. At 20 °C in ether or in THF medium, the major product was the acetylene **13**, together with allene **12** and a small amount of the dimer **7**. Thus the formation of cyclopropene **2** in this way was not useful, as confirmed by the low yield (maximum 13%) of **7**.

The situation improved dramatically when the dibromide *trans*-**11** was subjected to reaction with MeLi under the same conditions (Et_2O, −90 °C to −50 °C, 20 min) (Scheme 6). This reaction resulted in almost quantitative formation of cyclopropene **2** together with ca. 4% of the allene **12**. The cyclopropene **2** was again unstable but could be detected directly by ^{1}H NMR spectroscopy at −40 °C. Addition of cyclopentadiene (Cpd) to the reaction mixture at −50 °C allowed a single [4+2]-adduct **14** to be isolated in 92% yield based on starting *trans*-**11**.

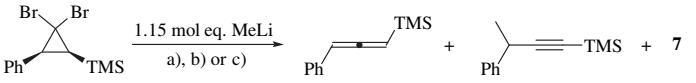
The results represented in Schemes 5 and 6 show that the formal *cis*- and *trans*-2,3-disubstituted trimethylsilylcyclopropylidene intermediates **16** (generated from **11** and MeLi) transform primarily either into allene **12** or 1-trimethylsilylcyclopropene **2**, respectively, and the balance is determined by the stereochemistry of Ph and TMS substituents in the starting dibromides **11** (Scheme 7). The formation of **2** from *trans*-**11** apparently occur through intermediates **15** and **16** by a lithium–bromine exchange followed by a formal loss of lithium bromide to give a cyclopropylidene, which rearranges by a 1,2-trimethylsilyl shift. The different outcomes from the *cis*- and *trans*-isomers **11** may simply reflect a steric effect of the Ph group slowing the migration of the trimethylsilyl-group in the *cis*-case and allowing the normal cyclopropylidene–allene rearrangement,[13] to compete to form **12**. A more subtle effect based on the stereochemistry of the lithium–bromine exchange in **15** or on the formation of a more complex intermediate such as carbenoids rather than 'free' carbenes is also possible.

The structure of adduct **14** was in accordance with its NMR spectra. The *endo*-configuration of the cyclopropane was determined based on an NOESY experiment, which showed the spatial interaction of the TMS group and the bridge protons at C^7. The *anti*-

In order to better understand ene-process, a route to the cyclopropene **2** was required, which could be carried out at low temperature to minimize the rate of its dimerization and to avoid undefined byproduct formation. It is known that reaction of 1,1-dibromo-2-trialkylsilylcyclopropanes with MeLi in ether at 20 °C or −90 °C leads to the formation of 1-trialkylsilylcyclopropenes due to the 1,2-trialkylsilyl shift in the intermediate cyclopropylidene.[11] To exploit this route, individual stereoisomeric dibromides *cis*-**11** and *trans*-**11** (Scheme 4) were prepared by dibromocyclopropanation of the corresponding (*Z*)- or (*E*)-1-phenyl-2-trimethylsilylethenes (*Z*)-, (*E*)-**10** available from acetylene **9** by stereoselective reduction with DIBAL-H.[12]



Scheme 4.

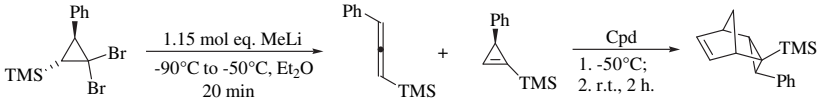


cis-**11** **12** **13**

a) Et_2O, -90 °C to -50 °C, 30 min:	97%	-	1%
b) Et_2O, 20 °C, 1 h:*	31%	56%	12%
c) THF, -90 °C to -50 °C, 20 min:*	38%	49%	13%

* yields by ^1H NMR spectroscopy

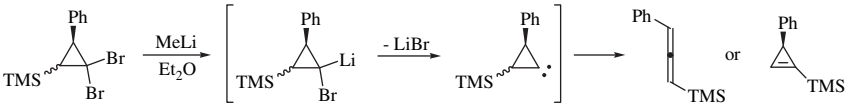
Scheme 5.



trans-**11** **12** (4%) **2** (96%) **14** (92%)

by ^1H NMR at -40 °C

Scheme 6.

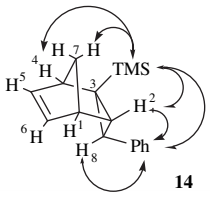


cis- or *trans*-**11** **15** **16** **12** from *cis*-**11** **2** from *trans*-**11**

Scheme 7.

orientation of the phenyl substituent was determined based on the *trans*-stereochemistry of H^2 and H^8 (J=3.2 Hz) and the interaction between TMS group and *ortho*-phenyl protons in the NOESY spectrum (Table 1).

Table 1
The results of NOESY experiment for adduct **14**



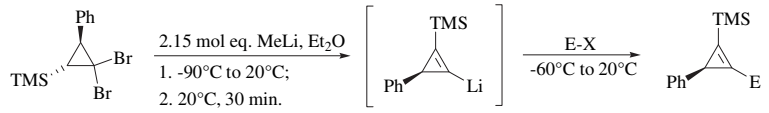
14

Proton	TMS	H^1	H^2	H^4	H^8
H^2	w	m			
H^4	s				
H^7	s	s	w	s	
o-Ph	m		s		w

Successful generation of cyclopropene **2** from *trans*-**11** provided a simple *one pot* route to 2-substituted 1-trimethylsilyl-3-phenylcyclopropenes. The *trans*-isomer **11** reacted with methyllithium (2.15 mol equiv, ether, −90 °C to 20 °C), leading to a lithium–hydrogen exchange in the intermediate **2** to produce lithiocyclopropene **17**. This was trapped by electrophiles (methyl iodide, trimethylsilyl chloride or carbon dioxide) to give the corresponding 3-phenylcyclopropenes **18**–**20**, mostly in good yields (Scheme 8). Quenching of lithiocyclopropene **17** with MeOD or D_2O afforded the unstable cyclopropene **3** in a high yield, proved by the analysis of its further ene-reaction products (see below), while the reaction of **17** with methyl chloroformate failed to lead to the corresponding cyclopropene ester.

If the cyclopropene **2** was worked up at 20 °C in the absence of a trap, the dimer **7** was again obtained, in this case accompanied by two trimers, **21** and **22** (Scheme 9). Compound **2** was relatively stable at −40 °C (an 11% solution in $CDCl_3$ of 50:41:5 monomer **2**/dimer **7**/trimer **21** immediately after reaction rearranged to a 23:56:14 mixture in 27 h) but had reacted completely in 12 h at rt either neat or as a 7% ethereal solution. Products **7** and **21** were isolated as individual compounds in 49% and 31% yield, respectively, while the minor trimer **22** was characterized only as a mixture with **21**.

The dimer **7** was efficiently trapped by reaction with cyclopentadiene to give a crystalline *endo*-adduct **23**, which was used for X-ray analysis (Fig. 1); this, in turn, allowed the relative stereochemistry of parent **7** to be determined. Compound **7** appeared to be inactive toward 1,3-DPIBF and furan at 20 °C; however, it easily formed single [3+2]-adducts **24** and **25** in reactions with benzo- and *p*-nitrobenzonitrile oxides generated in situ from the corresponding chlorides of hydroxamic acids and triethylamine.[14] Under

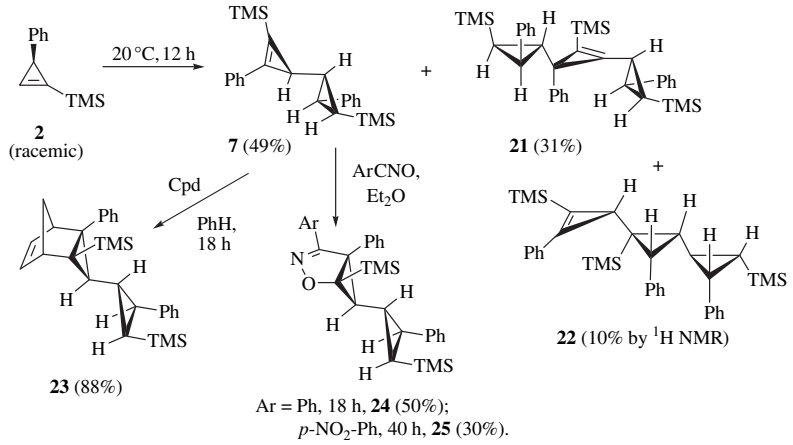


trans-**11** **17** **18-20**

E-X: MeOD (D_2O), MeI, TMSCl, CO_2, $ClCO_2Me$.

No	**18**	**19**	**20**
E	Me	TMS	COOH
%	97	90	57

Scheme 8.



Scheme 9.

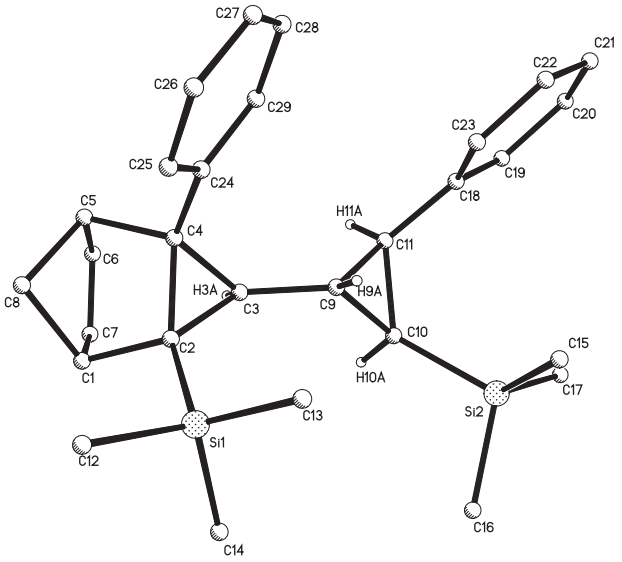
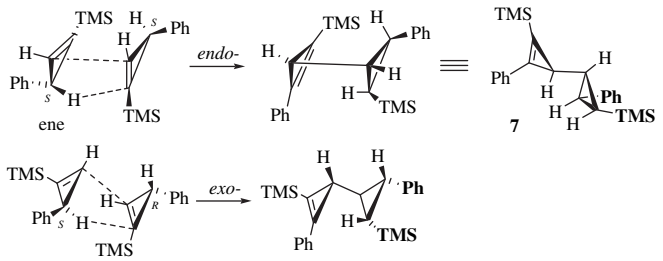


Figure 1. X-ray crystal structure of cyclopentadiene cycloadduct **23**.

these conditions neither of the trimers **21**, **22** reacted with the cyclopentadiene, 1,3-DPIBF, furan, diazomethane, and Ar-nitrile oxides.

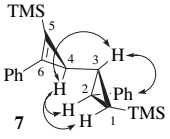
The X-ray crystal structure of the adduct **23** showed that the dimer **7** was formed from two identical molecules of **2**, rather than two enantiomeric molecules, and that the reaction occurred through an *endo*-transition state (Scheme 10, the only difference between the structures is marked bold). This, together with detailed NMR analysis allowed the correct structure of compounds **7**, **24** and **25** to be established.



Scheme 10.

The *cis*-orientation of protons H^1, H^2 and H^4 relative to C^1–C^2–C^3 of the cyclopropane ring of dimer **7** was confirmed by an NOESY experiment (Table 2). The strong interaction between H^3 and H^4 as well as the small coupling constant (J=4.1 Hz) are evidence for a deviation (up to 45°) of dihedral angle H^3–C^3–C^4–H^4 from a transoid conformation (180°) about the C^3–C^4 bond in solution.

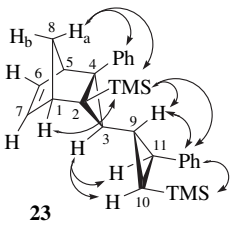
Table 2
The results of an NOESY experiment for dimer **7**



Proton	TMS_1	H^1	H^2	H^3
H^2		s		
H^4		s	s	s
o-Ph_2	w		s	s
o-Ph_6			m	

In comparison with the above situation for **7**, the preferred conformation around the C^3–C^9 bond in the cyclopentadiene adduct **23** (Table 3) is found to be *trans*- (angle H^3–C^3–C^9–H^9 close to 180°), both in the solid state (based on X-ray data, Fig. 1) and in solution (based on NMR experiments). In the latter case, this was determined from the relatively high coupling constant (J=9.7 Hz) between H^3 and H^9 along with the absence of spatial contact between them in the NOESY spectrum. Moreover, the NOESY data

Table 3
The results of an NOESY experiment for Cpd-adduct **23**

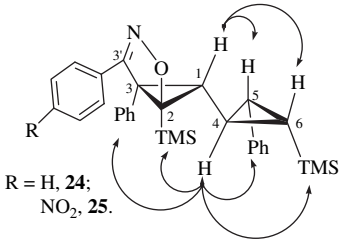


Proton	TMS_2	TMS_{10}	H^3	H^{8a}	H^9	H^{10}
H^1	m					
H^6			m			
H^{8a}	m					
H^9	m	w				
H^{10}		w	m			
H^{11}			s			s
o-Ph_{11}	s	s			s	
o-Ph_4	s	m		s		

afforded another confirmation, namely long-distance contacts between protons of TMS_2/*ortho*-Ph_{11} and TMS_{10}/*ortho*-Ph_4 groups.

The structure of adducts **24** and **25** was assigned on the basis of HSQC, HMBC and NOESY data. In particular, HMBC spectra of these compounds revealed the location of TMS groups at C^2 and C^6 due to the presence of correlation peaks CH_3–Si^2/C^2 and CH_3–Si^6/C^6 (Table 4). The location of phenyl residues was also established by HMBC-correlations between corresponding *ortho*-protons with carbon atoms C^3, $C^{3\prime}$ and C^5. The above results showed the formation of [3+2]-adducts occurred regiospecifically with the attack of the TMS-substituted atom of the cyclopropene double bond by the *O*-side of the nitrile oxide. The *cis*-orientation of H^4, Ph_3 and TMS_2 relative to C^1–C^2–C^3 ring and H^5, H^6 relative to C^4–C^5–C^6 was confirmed by NOESY experiments (Table 4). The absence of spatial contact H^1/H^4 revealed that the predominant conformer about the C^1–C^4 bond had a *trans*-orientation of protons H^1 and H^4 just as in the case of **23**. This conclusion was in agreement with the rather large values of the $^3J_{1,4}$ coupling constant (10 Hz). Thus, the addition of the nitrile oxide occurred stereospecifically from the less hindered side of the cyclopropene fragment of dimer **7**.[14a]

Table 4
The results of NOESY experiments for [3+2]-adducts **24**, **25**

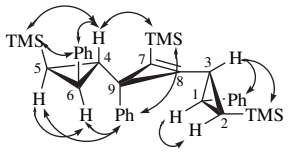


Proton	H^1	H^4	H^5	TMS_2
H^5	m			
H^6	s		s	
TMS_2		s		
TMS_6		w		
o-Ph_3		m	w	m
o-Ph_5		s	s	m

Unfortunately, neither of the trimers **21** or **22** was obtained as a crystalline derivative suitable for X-ray. However, as long as these products resulted from the reaction between **7** and **2**, then understanding the correct structure of **7** made the determination of the relative configuration of the trimers easier. For instance, after careful analysis of NMR data of the major trimer **21** it was found that there were only two possibilities for its formation from **7** and **2** (Scheme 11, the only difference between the structures is marked bold), but all attempts to solve this problem by NMR failed.

In accordance with the NOESY spectrum, protons H^1 and H^2 were *cis*-oriented relative to the C^1–C^2–C^3 ring; protons H^5, H^6 and Ph_9 were spatially close (Table 5). Groups of substituents Ph_1, TMS_2, H^3 and H^4, TMS_5, Ph_6 were *cis*-oriented relative to the C^1–C^2–C^3 and C^4–C^5–C^6 carbons of the cyclopropane rings, respectively. This information was in good agreement to the proposed ene-scheme of **21** formation, however at the same time it was not possible to determine the correct location of the TMS_5 and Ph_6 pair in the C^4–C^5–C^6 ring precisely (Scheme 11).

Table 5
The results of an NOESY experiment for trimer **21**



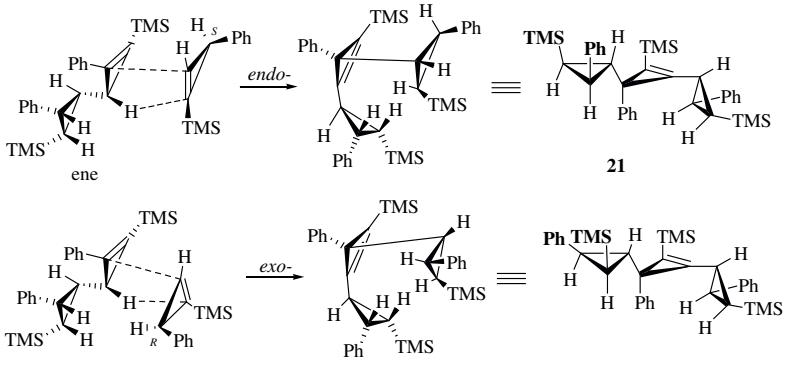
21

Proton	TMS_5	TMS_2	TMS_7	H^1	H^3	H^4	H^5	H^6
H^2				s				
H^3		s						
H^4	s		s					
H^6							s	
o-Ph_1		s		m	s			
o-Ph_6	s		s			s		m
o-Ph_9			s				m	m

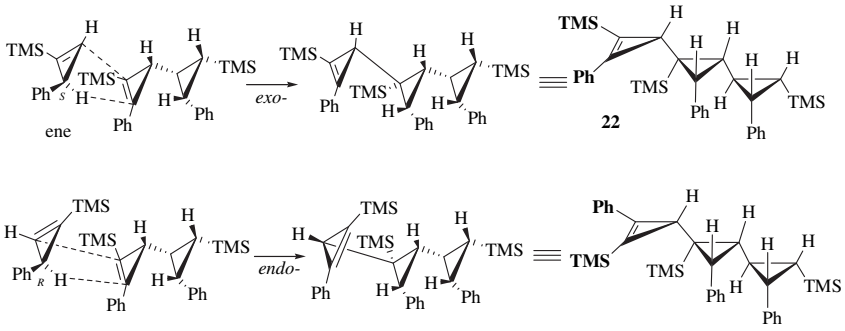
The situation with the minor trimer **22** was similar to that discussed above for **21**. Thus the proposed scheme of its formation again included two possible routes starting from **2** and **7** (Scheme 12, the only difference between the structures is marked in bold) but all attempts to exactly establish the regiochemistry of the TMS/Ph pair in the unsaturated ring failed.

To determine the correct routes to the trimers, it was decided to apply another approach resulting from Schemes 10–12. This required the introduction of chirality into the parent cyclopropene **2**, that in turn could clarify the details for the reaction between **7** and **2**. Since the formation of dimer **2** occurs within one enantiomeric series of **2**, then the formation of **21** from chiral **2** via **7** would require an *endo*-ene-process; the absence of **21** would suggest the opposite *exo*-transition state. The same picture can be observed for minor product **22**. Moreover, the formation of one isomer of **7** from **2** would create eight chiral centers in **23** from the single chiral center in **2**.

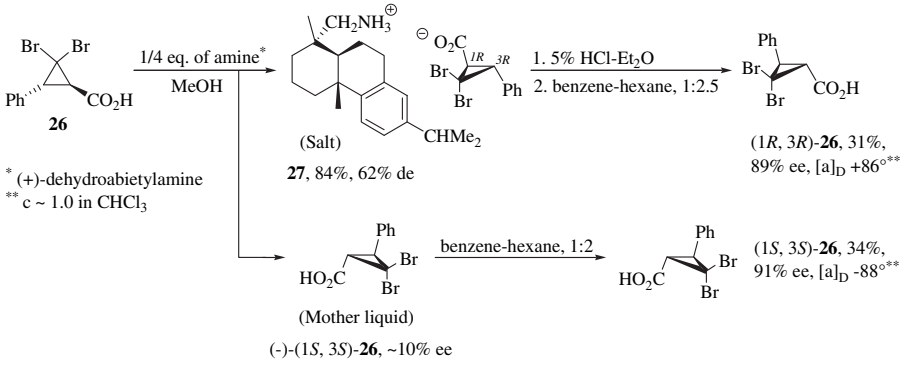
In order to exploit the above, the trimethylsilylcyclopropene (*S*)-**2** was obtained from the optically active acid (-)-(1*S*, 3*S*)-**26**, itself produced by resolution of racemic acid **26** using (+)-dehydroabiethylamine (Scheme 13).[15] The main steps of the resolution process included: a) formation and separation of a diastereomeric salt **27**, which was almost insoluble in common solvents and therefore wasn't subjected to recrystallization; b) recovery of enriched acid (+)-**26** (62% ee) from **27** and its subsequent further optical enrichment up to 89% ee by crystallization of racemic acid



Scheme 11.



Scheme 12.



Scheme 13.

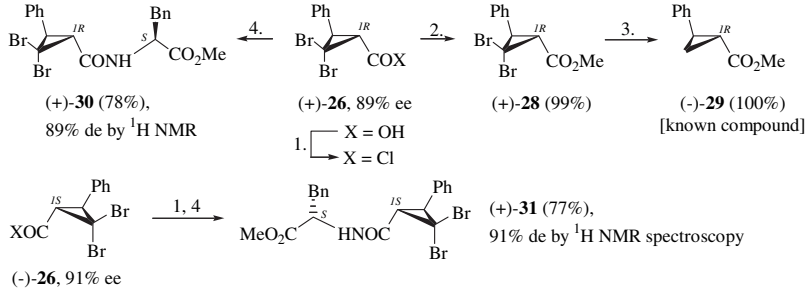
26 from benzene/hexane mixture; c) the acid (-)-**26** (10% ee) recovered from mother liquid was enriched to 91% ee analogously by precipitating of the parent racemate **26** from a benzene/hexane solution.

The absolute configuration of optically active acid (+)-**26** [(1*R*, 3*R*)-] was established by its two step transformation to methyl ester (-)-**29** with known [(1*R*, 2*R*)-] absolute stereochemistry.[16a] The enantiomeric excesses of chiral acids (+)- and (-)-**26** (89% and 91% ee, respectively) were determined based on the ^{1}H NMR spectroscopy data of their diastereomeric amides with L-β-phenylalanine methyl ester generated in situ from corresponding hydrochloride salt and triethylamine (Scheme 14).

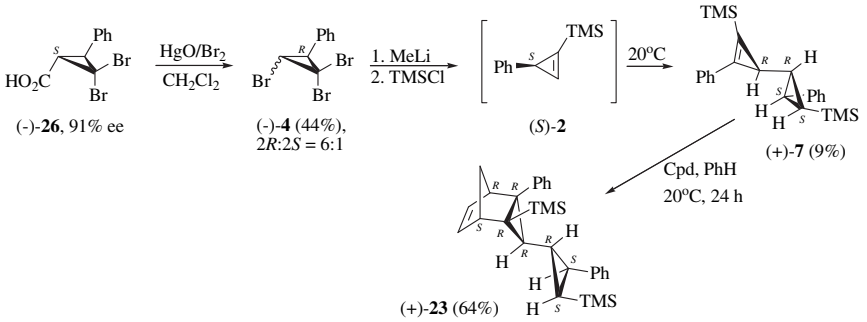
Optically active cyclopropene (*S*)-**2** was generated starting from acid (1*S*, 3*S*)-**26** (91% ee) according to Scheme 15, which included the preparation of tribromide (3*R*)-**4** followed by reaction with methyllithium and chlorotrimethylsilane.

Surprisingly, the dimer (+)-**7** was isolated in only low yield; trimers **21** and **22** were identified by NMR spectroscopy in a complex mixture with other undefined products. The reason for the difference between the reactions of the racemic and optically active cyclopropenes is the subject of further analysis and remains unknown up to now. However, the presence of two trimers derived from optically active monomer (*S*)-**2** indicates that they are made up of three identical monomer molecules, not of enantiomeric molecules. Trapping of (+)-**7** with cyclopentadiene gave a 64% yield of the adduct (+)-**23** of the corresponding enantiomerically enriched cyclopropene possessing eight chiral centers (Scheme 15).

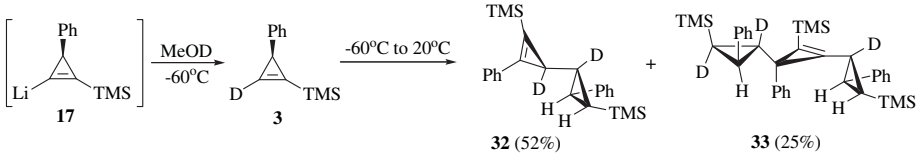
According to NMR data the structure of dimer (+)-**7** derived from the ene-reaction of (*S*)-**2** was that of one enantiomer of racemic **7** above, therefore the mechanisms of formation of (+)-**7** from (*S*)-**2** and **7** from **2** were the same and included an *endo*-transition state in the reaction between identical enantiomers of cyclopropene **2** (Scheme 10). The regiochemistry of the major trimer **21** was assigned based on an *endo*-transition state as in the *ene*-dimerisation, on the basis of the above requirement that the same enantiomer of the cyclopropene **2** must add to the dimer **7** (Scheme 11). On the other hand, the structure of the minor trimer **22** appears to require an *exo*-transition state (Scheme 12).



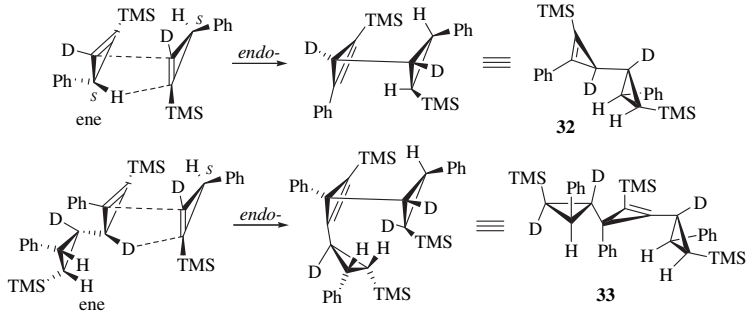
Scheme 14.



Scheme 15.



Scheme 16.



Scheme 17.

Attempts to trap the intermediate **17** with MeOD or D_2O, however, did not produce the deuterated cyclopropene **3**. Instead, the dimer **32** and trimer **33** were observed (Scheme 16). Even under the same conditions under which **2** had been observed directly by ^1H NMR spectroscopy (−40 °C, $CDCl_3$), no **3** could be observed, suggesting that the *ene*-dimerisation of the 2-D compound proceeds somewhat faster than that of the 2-H compound. It is worth also noting that only one trimer was observed from **3**, whereas two were formed in 3:1 ratio from **2**.

The structures of compounds **32**, **33** were similar to non-deuterated analogs **7** and **21,** respectively, and their formation apparently included the same *endo*-steps during the ene-sequence. One of the possible explanations of this unexpected reaction rate of 2-D-derivative **3** compared to **2** might be that it results from deuterium isotope effects. Thus, an inverse secondary isotope effect could be responsible for this in the dimerisation, which converts two pseudo-*sp* C–H(D) bonds into cyclopropane C–H(D) bonds.[6b,8] Obviously the formation of trimer **33** from **32** and **3** is more complicated process including the transfer of a D-atom from ene to enophile containing another deuterium at C-2 of the small ring (Scheme 17).

3. Conclusion

The introduction of a 1-trimethylsilyl-substituent leads to ene-dimerisation and trimerisation of 3-phenylcyclopropenes with a high degree of regio- and stereochemical control. By starting with a single enantiomer, seven new chiral centers are generated by ene-dimerisation/[4+2] cycloaddition sequence. The introduction of a deuterium at the 2-position of the cyclopropene leads to unusual changes in the stability of the cyclopropene and the balance of dimeric and trimeric products.

4. Experimental

4.1. General details

Commercial reagents were used without further purification unless stated. Diethyl ether and THF were distilled over sodium wire. Petroleum was of boiling point 40–60 °C. Benzohydroximinoyl and *p*-nitrobenzohydroximinoyl chlorides were prepared by NCS–DMF chlorination of the corresponding oximes.[17] Reactions requiring anhydrous conditions were performed using oven dried glassware (250 °C) that was cooled under either dry nitrogen or argon; experiments were conducted under a positive atmosphere of argon. Unless stated, organic solutions were dried over anhydrous magnesium sulfate and evaporated at 14 mm Hg; yields quoted are for purified compounds and any ratios given are calculated by comparing integrals in the ^1H NMR spectrum or by GLC data.

New compounds were homogenous by GLC or TLC. GLC was conducted using a Carlo Erba HRGC 5300 F.I.D. on a capillary column (30 m×0.32 mm id Phase, DB5 split ratio of 50:1) with nitrogen carrier gas. TLC was performed using Aldrich silica plates

coated with silica gel 60 (F254). Column chromatography was conducted with Matrex Silica 60 (Fisher Scientific Int. Co.) and Merck LiChroprep Si 60 under medium pressure. Melting points are uncorrected. Unless stated, infrared spectra were obtained as solutions in $CHCl_3$ or as liquid films on a Perkin Elmer 1600 FTIR spectrometer. Low resolution mass spectra were measured using a Finnigan 8430 spectrometer using EI 70 eV unless stated. Accurate mass measurements were carried out on a Micromass™ GCT spectrometer. Microanalyses were performed on a Carlo Erba Model 1106 CHN analyzer. Optical rotation was measured using IGP-01 polarimeter. NMR spectra were recorded in $CDCl_3$, using Bruker AC250 or A500 spectrometers at 250 MHz or 500 MHz (^{1}H) and 62.9 MHz or 125 MHz (^{13}C). ^{13}C spectra were broad-band decoupled and in most cases corresponding DEPT spectra were also recorded. All previously described compounds were characterized by IR, ^{1}H and ^{13}C NMR spectroscopy and gave data identical to those in the literature.

4.2. Generation and trapping of 1-trimethylsilyl-3-phenylcyclopropene (2) from tribromide 4

*4.2.1. 9-Trimethylsilyl-1,8,10-triphenyl-12-oxatetracyclo[6.3.1.0^{2,7}.0^{9,11}]-dodeca-2,4,6-triene (**6**).* Methyllithium in ether (1.42 mL, 1.85 mmol, 1.30 M, 2.2 mol equiv) was added dropwise to tribromide **4** (300 mg, 0.84 mmol) in dry ether (10 mL) at −82 to −80 °C over 3 min. The solution was stirred for 5 min at −80 °C and allowed to reach rt (20 min). After a further 30 min at rt the mixture was cooled to −60 °C and chlorotrimethylsilane (0.15 mL, 128 mg, 1.18 mmol, 1.4 mol equiv) was added dropwise. The mixture was stirred for 10 min at −60 °C and 30 min at rt, cooled to −50 °C, quenched with methanol (0.1 mL) and then 1,3-DPIBF (251 mg, 0.93 mmol, 1.1 mol equiv) in dry THF (4 mL) was added. The resulting solution was allowed to reach rt (15 min), stirred for 1 h and quenched with water (3 mL). The organic layer was separated, the aqueous layer was extracted with ether (2×5 mL). The combined organic layers were washed with brine (5 mL), dried and evaporated to give an orange oil (450 mg), which was dissolved in dry THF (4 mL) and added to a mixture of maleic anhydride (92 mg, 0.93 mmol) and Et_3N (310 mg, 3.07 mmol) in dry ether–THF mixture (1:1, 5 mL). The mixture was stirred for 35 min at rt, quenched with water (4 mL) and diluted with ether (5 mL). The organic layer was separated, the aqueous layer was extracted with ether (10 mL). The combined organic layers were extracted with 8% aq NaOH (4×10 mL), washed with brine (5 mL), dried and evaporated. Chromatography of the residue (214 mg) on silica (petrol–ether, 20:1, R_f 0.30) gave adduct **6** (115 mg, 0.25 mmol, 30%) as a white powder, mp 155–156 °C (aq MeOH) (Found M$^+$: 458.2049. $C_{32}H_{30}O^{28}Si$ requires: 458.2066), which showed δ_H: −0.53 (9H, s, TMS), 2.62 (1H, d, J=3.8 Hz, H-11), 3.77 (1H, d, J=3.8 Hz, H-10), 7.15–7.91 (19H, m, Ar); δ_C: 0.5, 29.9, 35.6, 37.5, 88.7, 94.3, 119.6, 122.0, 125.2, 126.1, 126.5, 128.2, 128.3, 128.44, 128.46, 129.0, 129.8, 136.1, 136.4, 138.9, 148.8, 151.3; υ_{max} ($CHCl_3$): 3061 m, 3029 m, 2952 m, 2894 w, 1952 w, 1811 w, 1604 m, 1497 s, 1454 s, 1339 w, 1298 s, 1250 s, 1217 m, 1110 w, 1075 w, 1050 w, 1024 m, 982 s, 871 m, 837 s, 750 s, 698 s cm^{-1}; *m*/*z*, %: 460 (M$^+$, ^{30}Si, 0.7), 459 (M$^+$, ^{29}Si, 2), 458 (M$^+$, ^{28}Si, 4.5), 386 (6), 385 (21), 353 (12), 352 (54), 339 (5), 338 (19), 337 (100), 322 (11), 321 (48), 291 (17), 276 (16), 263 (4), 215 (6), 202 (6), 160 (6), 107 (2), 106 (12), 105 (19), 77 (19), 73 (21), 59 (12).

*4.2.2. 3,3′-Diphenyl-2,2′-bis-trimethylsilylbicyclopropyl-2-ene (**7**).* Methyllithium in ether (2.05 mL, 2.87 mmol, 1.40 M, 2.2 mol equiv) was added dropwise to tribromide **4** (464 mg, 1.30 mmol) in dry ether (15 mL) at −82 to −80 °C over 4 min. The solution was stirred for 5 min at −80 °C and allowed to reach rt (20 min). After a further 30 min at rt the mixture was cooled to −60 °C and chlorotrimethylsilane (0.22 mL, 184 mg, 1.69 mmol, 1.3 mol equiv) was added dropwise. The mixture was stirred for 10 min at −60 °C and 1 h at rt, cooled to −40 °C and quenched with water (2 mL). The organic layer was separated, the aqueous layer was extracted with ether (2×7 mL). The combined organic layers were washed with brine (5 mL), dried and evaporated. This gave an orange oil (241 mg), which contained by ^{1}H NMR monomer **2** (30%), dimer **7** (20%) and cyclopropene **19** (10%). After 12 h at rt the neat sample was columned on silica (pentane) to yield dimer **7** (98 mg, 0.26 mmol, 40%, R_f 0.52, R_t 14.84 min) (Found M$^+$: 376.2035. $C_{24}H_{32}{}^{28}Si_2$ requires: 376.2043) and cyclopropene **19** (19 mg, 0.07 mmol, 5%, R_f 0.57) as colorless oils. Compound **7** showed δ_H: −0.28 (9H, s, TMS-2′), −0.01 (1H, dd, J=7.3, 10.4 Hz, H-2′), 0.36 (9H, s, TMS-2), 1.45 (1H, ddd, J=4.1, 4.7, 7.3 Hz, H-1′), 1.96 (1H, d, J=4.1 Hz, H-1), 2.20 (1H, dd, J=4.7, 10.4 Hz, H-3′), 7.23–7.62 (10H, m, Ph-3, Ph-3′); δ_C: −0.9, −0.6, 14.4, 23.5, 25.9, 27.6, 116.8, 125.6, 127.8, 128.63, 128.65, 129.2, 129.4, 130.7, 136.9, 141.5; υ_{max}: 3079 w, 3059 w, 3026 w, 2954 s, 2897 m, 1944 w, 1768 m, 1602 m, 1488 m, 1446 m, 1406 w, 1248 s, 1025 w, 930 m, 912 m, 840 s, 756 s, 691 s cm^{-1}; *m*/*z* (GC/MS), %: 378 (M$^+$, 0.6), 377 (M$^+$, ^{28}Si+^{29}Si, 1.3), 376 (M$^+$, $^{28}Si_2$, 4), 375 (M$^+$−1, 0.6), 319 (6), 304 (8), 303 (92), 302 (14), 288 (69), 287 (58), 273 (55), 271 (12), 230 (8), 229 (19), 228 (11), 211 (12), 187 (55), 159 (9), 145 (11), 135 (31), 128 (16), 74 (16), 73 (100), 59 (22). Compound **7** began to decompose after one night at −20 to 20 °C under an Ar atmosphere, but it was stable for months as a hexane solution at −20 °C. The spectral data of cyclopropene **19** were identical to those obtained in Section 4.6.3.

4.3. Synthesis of individual stereoisomers of dibromides *cis*-11 and *trans*-11

*4.3.1. 1-Phenyl-2-(trimethylsilyl)ethyne (**9**).* *n*-BuLi in hexane (35.4 mL, 53.8 mmol, 1.52 M, 1.1 mol equiv) was added dropwise to a freshly distilled phenylacetylene **8** (5.00 g, 49.0 mmol) in dry THF (50 mL) at −78 to −65 °C over 10 min. The mixture was stirred for 30 min at −78 °C and then chlorotrimethylsilane (7.5 mL, 6.4 g, 58.8 mmol, 1.2 mol equiv) was added dropwise at −78 to −65 °C over 10 min. After a further 30 min at −78 °C and 1 h at rt the solution was cooled to 0 °C and quenched with satd aq NH_4Cl (20 mL). The organic layer was separated, the aqueous layer was extracted with ether (2×30 mL). The combined organic phases were washed with brine (20 mL), dried and evaporated. Distillation afforded acetylene **9**[18] (7.68 g, 44.1 mmol, 90%) as a colorless oil, bp 79–80 °C at 2 mm Hg, which showed δ_H: 0.33 (9H, s, TMS), 7.35 (3H, m, Ph), 7.53 (2H, m, Ph); δ_C: −0.03, 94.0, 105.1, 123.1, 128.2, 128.4, 131.9; υ_{max}: 3080 m, 3057 m, 3032 m, 2958 s, 2898 s, 2488 w, 2158 s, 1948 w, 1893 w, 1804 w, 1753 w, 1598 s, 1573 m, 1488 s, 1444 s, 1408 m, 1343 w, 1281 m, 1249 s, 1219 s, 1176 w, 1156 w, 1069 s, 1027 s, 999 w, 931 m, 914 s, 862 s, 757 s, 690 s, 644 s cm^{-1}.

*4.3.2. cis-1-Phenyl-2-(trimethylsilyl)ethylene [(Z)-**10**].* DIBAL-H in hexane (46 mL, 46 mmol, 1.0 M, 1.4 mol equiv) was added dropwise to a solution of acetylene **9** (5.75 g, 33.0 mmol) in dry ether (30 mL) over 10 min. The reaction mixture was stirred for 50 h at rt and carefully quenched with ice-cold 10% aq H_2SO_4 (250 mL). The organic layer was separated, the aqueous layer was extracted with ether (3×50 mL). The combined organic layers were washed with brine (30 mL), dried and evaporated. Distillation of the residue gave alkene (*Z*)-**10**[12] (5.67 g, 32.2 mmol, 97%, R_t 2.82 min) as a colorless oil, bp 69–70 °C at 2 mm Hg, which showed δ_H: 0.15 (9H, s, TMS), 5.91 (1H, d, J=15.1 Hz, =CH), 7.32–7.39 (5H, m, Ph), 7.44 (1H, d, J=15.1 Hz, =CH); δ_C: 0.2, 127.3, 127.9, 128.1, 132.8, 140.1, 146.6; υ_{max}: 3058 w, 3023 w, 2957 s, 2897 w, 1592 m, 1571 m, 1492 m, 1444 w, 1247 s, 1072 w, 1027 w, 840 s, 773 m, 761 m, 702s cm^{-1}.

*4.3.3. trans-1-Phenyl-2-(trimethylsilyl)ethylene [(E)-**10**].* DIBAL-H in hexane (26.5 mL, 26.5 mmol, 1.0 M, 1.15 mol equiv) was added dropwise to a solution of acetylene **9** (4.0 g, 23.0 mmol) in dry

pentane (5 mL) over 5 min. The reaction mixture was stirred for 21 h at rt and carefully quenched with ice-cold 5% aq H_2SO_4 (100 mL). The organic layer was separated, the aqueous layer was extracted with ether (2×50 mL). The combined organic layers were washed with brine (30 mL), dried and evaporated. Distillation of the residue gave alkene (*E*)-**10**[12] (3.69 g, 20.9 mmol, 91%) as a colorless oil, bp 85–86 °C at 2 mm Hg, which showed δ_H: 0.23 (9H, s, TMS), 6.53 (1H, d, *J*=19.2 Hz, =CH), 6.92 (1H, d, *J*=19.2 Hz, =CH), 7.29–7.51 (5H, m, Ph); δ_C: −1.2, 126.4, 127.9, 128.5, 129.5, 138.4, 143.6; υ_{max}: 3101 w, 3077 m, 3059 m, 3023 m, 2988 m, 2955 s, 2896 m, 1940 w, 1874 w, 1801 w, 1605 s, 1574 s, 1493 s, 1447 s, 1332 w, 1247 s, 1214 m, 1196 m, 1070 w, 1028 w, 988 s, 869 s, 756 s, 723 s, 690 s cm^{-1}.

*4.3.4. cis-1,1-Dibromo-2-trimethylsilyl-3-phenylcyclopropane (cis-**11**).* Alkene (*Z*)-**10** (4.18 g, 23.7 mmol) was added to a mixture of bromoform (4.2 mL, 12.0 g, 47.4 mmol, 2 mol equiv), dichloromethane (10 mL) and *n*-hexadecyltrimethylammonium bromide (444 mg, 1.19 mmol, 5 mol %). The mixture was stirred vigorously and sodium hydroxide (9.5 g, 237 mmol, 10 mol equiv) in water (10 mL) was added over 5 min at below 31 °C. After 17 h at rt water (40 mL) was added and the mixture was extracted with dichloromethane (4×40 mL). The combined organic layers were washed with water (30 mL) and solvent was removed. The residue was dissolved in petrol–ether mixture (1:1, 200 mL) and filtered through Celite. Removal of the solvent and unreacted bromoform at 30–40 °C and 0.5 mm Hg gave a brown oil (9.46 g), which was columned on silica (petrol, R_f 0.45, R_t 7.03 min) to yield dibromide *cis*-**11** (7.40 g, 21.2 mmol, 90%) as a colorless oil (Found M^+: 347.9335. $C_{12}H_{16}{}^{30}Si^{79}Br_2$ requires: 347.9356), which showed δ_H: 0.13 (9H, s, TMS), 1.48 (1H, d, *J*=13.2 Hz, C*H*TMS), 3.24 (1H, d, *J*=13.2 Hz, C*H*Ph), 7.28–7.46 (5H, m, Ph); δ_C: −0.06, 30.4, 32.3, 38.9, 127.3, 127.9, 130.2, 135.8; υ_{max}: 3085 m, 3058 m, 3026 m, 2955 s, 2897 s, 1939 w, 1879 w, 1804 w, 1602 m, 1496 s, 1445 s, 1409 m, 1364 m, 1311 w, 1253 s, 1168 w, 1145 m, 1076 w, 1062 m, 1030 s, 1019 s, 965 s, 914 w, 842 s, 803 s, 766 s, 732 s, 697 s, 654 s cm^{-1}; *m*/*z*, %: 352 (M^+, $^{81}Br+^{81}Br+^{30}Si$, 0.12), 350 (M^+, 0.04), 348 (M^+, 0.04), 346 (M^+, $^{79}Br+^{79}Br+^{28}Si$, 0.14), 273 (1), 188 (20), 173 (10), 145 (9), 115 (64), 86 (11), 84 (18), 73 (100).

*4.3.5. trans-1,1-Dibromo-2-trimethylsilyl-3-phenylcyclopropane (trans-**11**).* Dibromide *trans*-**11** was prepared in a similar way to the previous experiment from alkene (*E*)-**10** (3.0 g, 17.0 mmol), bromoform (3.0 mL, 8.59 g, 34.0 mmol, 2 mol equiv), *n*-hexadecyltrimethylammonium bromide (310 mg, 0.85 mmol, 5 mol %) dissolved in dichloromethane (7 mL) and sodium hydroxide (6.8 g, 170 mmol, 10 mol equiv) in water (7 mL). After 15 h of vigorous stirring at rt and standard work up the organic residue (7.01 g) was columned on silica (petrol, R_f 0.34) to yield *trans*-**11** (5.19 g, 14.9 mmol, 88%) as a greenish oil, which crystallized in a white crystal mass, mp 20–21 °C (Found M^+: 347.9346. $C_{12}H_{16}{}^{30}Si^{79}Br_2$ requires: 347.9356) and showed δ_H: 0.30 (9H, s, TMS), 1.36 (1H, d, *J*=10.7 Hz, C*H*TMS), 2.85 (1H, d, *J*=10.7 Hz, C*H*Ph), 7.29–7.42 (5H, m, Ph); δ_C: −1.33, 27.4, 34.5, 39.1, 127.5, 128.2, 128.7, 137.1; υ_{max}: 3086 w, 3060 m, 3029 m, 2953 s, 2896 m, 1943 w, 1872 w, 1798 w, 1602 m, 1496 s, 1448 s, 1409 w, 1368 m, 1312 w, 1250 s, 1207 m, 1176 w, 1105 w, 1080 m, 1054 m, 1034 s, 1024 s, 1002 w, 954 s, 911 w, 846 s, 814 m, 785 m, 755 s, 717 m, 695 s, 620 m cm^{-1}; *m*/*z*, %: 350 (M^+, 0.004), 348 (M^+, 0.003), 346 (M^+, $^{79}Br+^{79}Br+^{28}Si$, 0.001), 270 (1), 269 (4), 268 (3), 267 (4), 266 (2), 196 (12), 194 (13), 188 (46), 173 (20), 145 (27), 139 (30), 137 (29), 115 (100), 89 (12), 73 (96).

4.4. Reactions of *cis*-1,1-dibromo-2-trimethylsilyl-3-phenylcyclopropane (*cis*-11) with MeLi

*4.4.1. 1-Trimethylsilyl-3-phenylpropadiene-1,2 (**12**).* Methyllithium in ether (0.72 mL, 1.0 mmol, 1.40 M, 1.15 mol equiv) was added dropwise to dibromide *cis*-**11** (300 mg, 0.86 mmol) in dry ether (10 mL) at −92 to −90 °C over 2 min. The mixture was stirred for 30 min at −90 °C, allowed to reach −50 °C (20 min) and carefully quenched with water (2 mL). The organic layer was separated, the aqueous layer was extracted with ether (5 mL). The combined organic layers were washed with brine (3 mL), dried and evaporated to give allene **12**[19] (157 mg, 0.83 mmol, 97%, R_t 7.87 min) as a colorless oil, which showed δ_H: 0.22 (9H, s, TMS), 5.46 (1H, d, *J*=6.7 Hz,=CH), 5.90 (1H, d, *J*=6.7 Hz,=CH), 7.15–7.36 (5H, m, Ph); δ_C: −0.8, 87.0, 87.9, 125.9, 128.6, 135.1, 210.2; υ_{max}: 3061 m, 3028 s, 2956 s, 2896 s, 1923 s, 1597 s, 1495 s, 1455 s, 1408 m, 1375 m, 1248 s, 1181 s, 1078 m, 1027 m, 907 s, 842 s, 768 s, 697 s, 631 s cm^{-1}; *m*/*z* (GC/MS), %: 190 (M^+, ^{30}Si, 0.8), 189 (M^+, ^{29}Si, 2.9), 188 (M^+, ^{28}Si, 14.4), 173 (3), 145 (8), 115 (9), 89 (5), 75 (5), 74 (10), 73 (100); R_f 0.57 (pentane). The presence of ~1% of dimer **7** in **12** was determined by GC/MS.

*4.4.2. The same reaction at rt, 1-trimethylsilyl-3-phenyl-3-methylpropyne-1 (**13**).* Methyllithium in ether (0.72 mL, 1.0 mmol, 1.40 M, 1.15 mol equiv) was added dropwise to dibromide *cis*-**11** (300 mg, 0.86 mmol) in dry ether (10 mL) at rt over 3 min. The mixture was stirred for 1 h at rt and carefully quenched with water (2 mL). The organic layer was separated, the aqueous layer was extracted with ether (5 mL). The combined organic layers were washed with brine (3 mL), dried and evaporated. This gave an yellowish oil (159 mg), which contained compounds **12** (31%), **13** (56%) and dimer **7** (12%). Part of the residue (124 mg) was columned on silica (pentane) to give allene **12** (38 mg, 23%, R_f 0.57) and a mixture of acetylene **13**[20] and dimer **7** (34 mg, 17%, ratio **13**/**7**=4/1 by ^1H NMR, R_f 0.44) as colorless oils. Acetylene **13** showed δ_H: 0.23 (9H, s, TMS), 1.53 (3H, d, *J*=6.9 Hz, Me), 3.83 (1H, q, *J*=6.9 Hz, C*H*Me), 7.24–7.62 (5H, m, Ph); δ_C: 0.2, 24.6, 32.8, 86.2, 109.5, 126.6, 126.9, 128.5, 143.0; υ_{max}: 3084 w, 3062 w, 3028 m, 2958 s, 2897 m, 2166 s, 1601 m, 1494 s, 1450 s, 1407 w, 1296 w, 1249 s, 1098 m, 1007 m, 917 s, 844 s, 759 s, 735 s, 698 s cm^{-1}; *m*/*z* (GC/MS), %: 204 (M^+, ^{30}Si, 1), 203 (M^+, ^{29}Si, 3.3), 202 (M^+, ^{28}Si, 19), 189 (4), 188 (15), 187 (80), 161 (2), 160 (6), 159 (34), 147 (2), 146 (3), 145 (22), 128 (11), 115 (6), 86 (21), 83 (30), 73 (100), 59 (31), 53 (9); R_t 7.58 min.

4.4.3. The same reaction in THF at −90 °C. Methyllithium in ether (0.72 mL, 1.0 mmol, 1.40 M, 1.15 mol equiv) was added dropwise to dibromide *cis*-**11** (300 mg, 0.86 mmol) in dry THF (10 mL) at −90 °C over 2 min. The mixture was stirred for 20 min at −90 °C, allowed to reach −50 °C (20 min) and quenched with water (2 mL). The organic layer was separated, the aqueous layer was extracted with ether (5 mL). The combined organics were washed with brine (3 mL), dried and evaporated. It gave yellowish oil (160 mg), which contained allene **12** (38%), acetylene **13** (49%) and dimer **7** (13%).

4.5. Generation and trapping of 1-trimethylsilyl-3-phenylcyclopropene (2) from dibromide *trans*-11

*4.5.1. 1-Trimethylsilyl-3-phenylcyclopropene (**2**).* Methyllithium in ether (0.72 mL, 1.0 mmol, 1.40 M, 1.15 mol equiv) was added dropwise to dibromide *trans*-**11** (300 mg, 0.86 mmol) in dry ether (10 mL) at −92 to −90 °C over 3 min. The mixture was stirred for 15 min at −90 °C, allowed to reach −50 °C (10 min) and carefully quenched with water (1 mL). The organic layer was quickly decanted and concentrated at −20 °C. It gave a colorless oil (161 mg), which contained by ^1H NMR at −40 °C 50% of monomer **2**, 41% of dimer **7**, 5% of trimer **21** and 4% of allene **12**. Cyclopropene **2** showed at −40 °C (11% solution in $CDCl_3$) δ_H: 0.28 (9H, s, TMS), 2.61 (1H, s, H-3), 7.17–7.56 (6H, m, H-2, Ph); δ_C: −1.3, 20.2, 116.7, 119.6, 124.7, 125.0, 127.7, 148.4; υ_{max}: 3079 w, 3059 w, 3025 m, 2955 s,

2897 m, 1693 s, 1602 m, 1492 m, 1446 s, 1407 w, 1248 s, 1070 w, 841 s, 756 s, 698 s cm^{-1}. The optimized syntheses of allene **12** and ene-products **7** and **21** see in Sections 4.4.1 and 4.7.1 correspondingly.

*4.5.2. 2-Trimethylsilyl-3-anti-phenyltricyclo[3.2.1.0^{2,4}]octene-6 (**14**).* Methyllithium in ether (1.0 mL, 1.03 mmol, 0.97 M, 1.2 mol equiv) was added dropwise to dibromide *trans*-**11** (300 mg, 0.86 mmol) in dry ether (10 mL) at −92 to −90 °C over 2 min. The mixture was stirred for 15 min at −90 °C, allowed to reach −50 °C (20 min), carefully quenched with methanol (0.15 mL), and then freshly distilled cyclopentadiene (0.36 mL, 284 mg, 4.3 mmol, 5 mol equiv) was added dropwise. The resulting solution was stirred for 2 h at rt and quenched with water (2 mL). The organic layer was separated, the aqueous layer was extracted with ether (3 mL). The combined organic phases were washed with water (3 mL), dried and evaporated. Chromatography of the residue (260 mg) on silica (petrol, R_f 0.57) afforded adduct **14** (202 mg, 0.79 mmol, 92%) as a colorless oil (Found: C 80.05, H 8.91, Si 11.48%. $C_{17}H_{22}Si$ requires: C 80.25, H 8.72, Si 11.03%), which showed δ_H: −0.25 (9H, s, TMS), 1.56 (2H, s, 2×H-bridge), 1.77 (1H, d, J=3.2 Hz, H-3), 2.04 (1H, t, J=3.8 Hz, H-4), 2.88 (1H, s, H-1), 2.95 (1H, s, H-5), 5.78 (1H, m, =CH), 5.88 (1H, m, =CH), 7.07–7.22 (5H, m, Ph); δ_C: −0.8, 16.1, 22.6, 38.1, 42.9, 47.2, 61.9, 125.7, 127.7, 129.4, 130.7, 131.3, 140.4; υ_{max}: 3135 w, 3090 w, 3065 m, 3035 m, 2975 s, 2940 s, 2880 s, 1600 m, 1500 m, 1452 m, 1406 w, 1382 w, 1331 m, 1255 s, 1195 w, 1170 m, 1120 w, 1091 m, 1080 w, 1030 m, 993 m, 962 m, 943 w, 915 m, 890 s, 880 s, 860 s, 842 s, 800 w, 758 s, 748 s, 710 s.

4.6. Synthesis of 1-trimethylsilyl-2-R-3-phenylcyclopropenes 18–20

*4.6.1. Preparation of an ethereal solution 1-trimethylsilyl-2-lithio-3-phenylcyclopropene (**17**).* Methyllithium in ether (1.32 mL, 1.85 mmol, 1.40 M, 2.15 mol equiv) was added dropwise to *trans*-**11** (300 mg, 0.86 mmol) in dry ether (10 mL) at −92 to −90 °C over 3 min. The mixture was stirred for 20 min at −90 °C and allowed to reach rt. After a further 30 min at rt the prepared solution of **17** was cooled to −60 °C and used directly for reactions with electrophiles (MeI, TMSCl, CO_2, and $ClCO_2Me$).

*4.6.2. 1-Trimethylsilyl-2-methyl-3-phenylcyclopropene (**18**).* Methyl iodide (0.5 mL, 1.14 g, 8.0 mmol, 9.3 mol equiv) was added dropwise to an ethereal solution of **17** at −60 °C. The mixture was allowed to reach rt, stirred for 5 h, cooled to 0 °C and quenched with water (2 mL). The organic layer was separated, the aqueous layer was extracted with ether (2×5 mL). The combined organic layers were washed with brine (3 mL), dried and evaporated to afford cyclopropene **18** (169 mg, 0.84 mmol, 97%) as a colorless oil (Found M^+: 202.1178. $C_{13}H_{18}{}^{28}Si$ requires: 202.1178), which showed δ_H: 0.19 (9H, s, TMS), 2.23 (3H, s, Me), 2.48 (1H, s, H-3), 7.04–7.29 (5H, m, Ph); δ_C: −0.9, 11.5, 24.5, 108.3, 124.4, 125.1, 127.8, 128.6, 148.3; υ_{max}: 3060 m, 3024 s, 2956 s, 1807 s, 1597 m, 1492 s, 1451 m, 1249 s, 1157 m, 1024 w, 999 w, 841 s, 758 s, 698 s cm^{-1}; m/z, %: 204 (M^+, ^{30}Si, 3), 203 (M^+, ^{29}Si, 10), 202 (M^+, ^{28}Si, 100), 187 (49), 185 (29), 169 (9), 159 (46), 143 (10), 129 (8), 128 (47), 127 (15), 114 (10); R_f 0.50 (pentane).

*4.6.3. 1,2-Ditrimethylsilyl-3-phenylcyclopropene (**19**).* Chlorotrimethylsilane (0.13 mL, 112 mg, 1.03 mmol, 1.2 mol equiv) was added dropwise to an ethereal solution of **17** at −60 °C. The mixture was allowed to reach rt, stirred for 2 h, cooled to 0 °C and quenched with water (2 mL). The organic layer was separated, the aqueous layer was extracted with ether (2×5 mL). The combined organic phases were washed with brine (3 mL), dried and evaporated to provide cyclopropene **19** (202 mg, 0.78 mmol, 90%) as yellowish oil (Found M^+: 262.1394. $C_{15}H_{24}{}^{28}Si^{30}Si$ requires: 262.1385), which showed δ_H: 0.20 (18H, s, 2×TMS), 2.42 (1H, s, H-3), 7.00–7.24 (5H, m, Ph); δ_C: −1.0, 22.0, 124.1, 124.9, 127.5, 130.8, 149.6; υ_{max}: 3078 w, 3060 w, 3024 m, 2957 s, 2897 m, 1940 w, 1879 w, 1725 s, 1597 s, 1492 s, 1451 m, 1406 w, 1250 s, 1212 w, 1078 w, 928 m, 902 m, 840 s, 757 s, 698 s cm^{-1}; m/z, %: 264 (M^+, ^{30}Si+^{30}Si, 0.2), 261 (M^+, ^{28}Si+^{29}Si, 0.2), 260 (M^+, ^{28}Si+^{28}Si, 0.8), 230 (2), 229 (5), 207 (8), 172 (5), 159 (5), 135 (5), 105 (8), 77 (17), 75 (30), 73 (100); R_f 0.57 (pentane).

*4.6.4. 1-Trimethylsilyl-3-phenylcyclopropene-2-carboxylic acid (**20**).* Dry gaseous CO_2 was passed through the stirred ethereal solution of **17** for 20 min at −60 °C and 20 min during for which the reaction mixture was allowed to reach 5 °C. Then the solution was cooled to −40 °C and quenched with water (4 mL). The organic layer was separated, the aqueous layer was extracted with ether (5 mL), acidified with cold 1 M aq HCl, and the product was extracted with ether (2×10 mL). The combined organic layers were washed with brine (5 mL), dried and evaporated to give acid **20** (113 mg, 0.48 mmol, 57%) as a white powder, mp 75–77 °C (Found M^+: 232.0927. $C_{13}H_{16}O_2{}^{28}Si$ requires: 232.0920), which showed δ_H: 0.26 (9H, s, TMS), 3.07 (1H, s, H-3), 7.09–7.31 (5H, m, Ph), 11.77 (1H, br s, CO_2H); δ_C: −1.6, 27.1, 123.4, 125.6, 125.9, 128.1, 138.8, 144.1, 167.1; υ_{max} ($CHCl_3$): 3500–2350 br s, 3061 s, 3028 s, 2960 s, 2900 s, 1945 w, 1873 w, 1784 s, 1681 s, 1604 s, 1493 s, 1453 m, 1405 s, 1252 s, 1217 s, 1138 s, 1074 w, 1014 m, 951 m, 907 m, 848 s, 761 s, 698 s cm^{-1}; m/z, %: 234 (M^+, ^{30}Si, 0.08), 233 (M^+, ^{29}Si, 0.2), 232 (M^+, ^{28}Si, 1.3), 231 (1), 217 (1.5), 216 (1), 202 (6), 188 (21), 187 (86), 173 (62), 172 (83), 159 (19), 145 (26), 142 (17), 130 (6), 128 (9), 115 (12), 114 (43), 105 (19), 102 (10), 77 (17), 75 (100), 73 (84).

4.7. *Ene*-di- and trimerisation of 1-trimethylsilyl-3-phenylcyclopropene (2) and its 2-D-derivative 3

*4.7.1. 3,3′-Diphenyl-2,2′-bis-trimethylsilylbicyclopropyl-2-ene (**7**), 2,1′,2″-triphenyl-3,3′,3″-tris-trimethylsilyl[1,1′;2′,1″]tercyclopropan-2′-ene (**21**) and 3,3′,3″-triphenyl-2,1′,2″-tris-trimethylsilyl[1,1′;2′,1″]-tercyclopropan-2-ene (**22**).* Methyllithium in ether (2.9 mL, 3.2 mmol, 1.12 M, 1.15 mol equiv) was added dropwise to dibromide *trans*-**11** (970 mg, 2.79 mmol) in dry ether (15 mL) at −92 to −90 °C over 3 min. The mixture was stirred for 15 min at −90 °C, allowed to reach −50 °C (20 min) and carefully quenched with water (3 mL). The organic layer was separated, the aqueous layer was extracted with ether (7 mL). The combined organic layers were washed with brine (5 mL), dried, and evaporated to give brown oil (534 mg), which was left for overnight (12–15 h) at rt under Ar atmosphere. This material was then columned on silica (hexane, ratio **21**/**22**=3:1 by ^{1}H NMR before the column) to give allene **12** (19 mg, 0.1 mmol, 4%, R_f 0.57), dimer **7** (257 mg, 0.67 mmol, 49%, R_f 0.52) as colorless oils; and trimer **21** (163 mg, 0.29 mmol, 31%, R_f 0.38) (Found M^+: 565.3054. $C_{36}H_{48}{}^{28}Si_2{}^{29}Si$ requires: 565.3060) as viscous colorless oil. The major trimer **21** showed δ_H: −0.37 (9H, s, TMS-3), −0.16 (1H, dd, J=6.9, 10.4 Hz, H-3), −0.14 (9H, s, TMS-3″), 0.14 (9H, s, TMS-3′), 0.78 (1H, dd, J=6.6, 10.7 Hz, H-3″), 1.80 (1H, dd, J=5.1, 6.9 Hz, H-1), 2.12 (1H, dd, J=5.1, 10.4 Hz, H-2), 2.59 (1H, dd, J=4.7, 6.6 Hz, H-1″), 2.79 (1H, dd, J=4.7, 10.7 Hz, H-2″), 7.12–7.59 (15H, m, Ph-2, Ph-1′, Ph-2″); δ_C: −0.96, −0.72, −0.65, 13.1, 17.78, 17.84, 23.2, 26.1, 28.8, 31.6, 110.6, 123.3, 125.6, 126.5, 126.8, 127.8, 128.1, 128.2, 128.6, 129.3, 131.0, 131.1, 139.2, 141.6; υ_{max}: 3060 w, 3027 w, 2953 s, 2896 w, 1940 w, 1840 m, 1601 m, 1496 m, 1445 m, 1402 w, 1247 s, 1155 w, 1009 w, 980 m, 909 s, 839 s, 756 s, 735 s, 699 s cm^{-1}; m/z, %: 567 (M^+, 0.08), 566 (M^+, ^{28}Si+^{29}Si$_2$, 0.3), 565 (M^+, ^{28}Si$_2$+^{29}Si, 0.8), 564 (M^+, ^{28}Si$_3$, 2), 492 (12), 491 (38), 418 (5), 417 (14), 403 (20), 401 (13), 375 (6), 344 (23), 313 (12), 287 (33), 286 (20), 270 (9), 265 (6), 159 (8), 135 (30), 91 (4), 75 (71), 73 (100), 59 (11). The minor trimer **22** (10% yield by ^{1}H NMR of the crude reaction mixture, R_f 0.35) was inseparable from **21** therefore was

characterized only as a mixture with latter and showed δ_H: −0.19 (9H, s, TMS), 0.20 (9H, s, TMS), 0.30 (1H, dd, *J*=6.9, 10.4 Hz, H-2″), 0.37 (9H, s, TMS), 1.53 (1H, ddd, *J*=4.4, 4.7, 6.9 Hz, H-1″ 1.59 (1H, dd, *J*=4.4, 8.8 Hz, H-2′), 1.79 (1H, d, *J*=8.8 Hz, H-3′), 2.28 (1H, dd, *J*=4.7, 10.4 Hz, H-3″), 2.48 (1H, s, H-1), 7.13–7.65 (15H, m, Ph-3, Ph-3′, Ph-3″); δ_C: −0.28, −0.06, 0.83, 18.9, 19.4, 20.6, 26.9, 28.4, 29.6, 32.9, 115.2, 125.62, 125.75, 130.9, 136.5, 139.7, 140.4. The spectral data of dimer **7** and allene **12** were identical to that obtained above in Sections 4.2.2 and 4.4.1, respectively.

*4.7.2. 1,1′-Dideutero-3,3′-diphenyl-2,2′-bis-trimethylsilylbicyclopropyl-2-ene (**32**) and 1,2,1″-trideutero-3,1′,3″-triphenyl-2,3′,2″-tris-trimethylsilyl[1,1′;2′,1″]tercyclopropan-2′-ene (**33**).* MeOD (0.15 mL) was added dropwise to an ethereal solution of **17** (Section 4.6.1) at −60 °C, allowed to reach rt and diluted with water (1 mL). The organic layer was separated, the aqueous layer was extracted with ether (5 mL). The combined organic layers were washed with brine (3 mL), dried and evaporated. Chromatography of the part of residue (101 mg from 161 mg) on silica (pentane) gave pure dimer **32** (53 mg, 0.14 mmol, 52%, R_f 0.39) (Found M^+: 381.2141. $C_{24}H_{30}D_2{}^{29}Si{}^{30}Si$ requires: 381.2148) and trimer **33** (26 mg, 0.046 mmol, 25%, R_f 0.26) (Found M^+: 567.3243. $C_{36}H_{45}D_3{}^{28}Si_3$ requires: 567.3252) as viscous colorless oils. Compound **32** showed δ_H: −0.26 (9H, s, TMS-2′), −0.01 (1H, d, *J*=10.4 Hz, H-2′), 0.37 (9H, s, TMS-2), 2.21 (1H, d, *J*=10.4 Hz, H-3′), 7.18–7.64 (10H, m, Ph-3, Ph-3′); δ_C: −0.8, −0.6, 14.3, 22.9 (t, *J*=25.7 Hz), 25.4 (t, *J*=23.5 Hz), 27.5, 116.6, 125.6, 127.8, 128.63, 128.65, 129.2, 129.4, 130.7, 136.8, 141.5; υ_{max}: 3078 w, 3059 w, 3026 w, 2954 s, 2896 m, 2166 w, 1944 w, 1766 s, 1602 s, 1488 m, 1446 m, 1406 w, 1248 s, 1098 w, 1028 w, 1000 w, 979 m, 916 m, 841 s, 755 s, 698 s cm^{-1}; *m/z*, %: 381 (M^+, $^{29}Si+^{30}Si$, 0.4), 380 (M^+, 2), 379 (M^+, $^{28}Si+^{29}Si$, 4.6), 378 (M^+, $^{28}Si_2$, 13), 377 (M^+−1, 7), 376 (6), 318 (5), 306 (9), 305 (43), 304 (34), 303(33), 290 (34), 289 (53), 288 (44), 275 (27), 274 (19), 273 (34), 272 (15), 271 (12), 232 (49), 231 (90), 230 (100), 229 (88), 228 (50), 216 (30), 215 (22), 203 (20), 202 (17), 159 (35), 135 (36), 105 (19). Compound **33** showed δ_H: −0.37 (9H, s, TMS), −0.14 (9H, s, TMS), 0.15 (9H, s, TMS), 0.77 (1H, d, *J*=10.7 Hz, H-2″), 2.13 (1H, s, H-3), 2.79 (1H, d, *J*=10.7 Hz, H-3″), 7.13–7.47 (15H, m, Ph-3, Ph-1′, Ph-3″); δ_C: −0.97, −0.75, −0.68, 12.9, 17.6, 17.7, 22.9, 26.0, 28.6, 31.5, 110.5, 123.2, 125.5, 126.4, 126.8, 127.8, 128.06, 128.16, 128.6, 129.3, 131.0, 131.1, 139.2, 141.5; υ_{max}: 3079 m, 3059 m, 3027 s, 2952 s, 2895 m, 2212 w, 1942 w, 1840 s, 1601 s, 1496 s, 1445 s, 1403 m, 1247 s, 1155 w, 1071 m, 1030 m, 1001 w, 984 m, 966 m, 894 m, 837 s, 756 s, 698 s cm^{-1}; *m/z*, %: 570 (M^+, $^{29}Si_3$, 0.06), 569 (M^+, $^{28}Si+^{29}Si_2$, 0.2), 568 (M^+, $^{28}Si_2+^{29}Si$, 0.5), 567 (M^+, $^{28}Si_3$, 1), 566 (M^+−1, 0.8), 565 (0.3), 564 (0.06), 495 (3), 494 (12), 493 (8), 419 (3), 405 (5), 404 (7), 403 (3), 345 (2), 328 (2), 316 (3), 315 (3), 301 (2), 288 (3), 254 (1), 159 (2), 135 (23), 105 (10), 77 (20), 75 (77), 73 (100).

*4.7.3. 2-Phenyl-anti-3-(2-phenyl-3-trimethylsilylcyclopropyl)-4-trimethylsilyltricyclo[3.2.1.0^{2,4}]oct-6-ene (**23**).* The mixture of dimer **7** (70 mg, 0.19 mmol) and freshly distilled cyclopentadiene (40 mg, 0.56 mmol, 3.0 mol equiv) in benzene (2 mL) was stirred for 18 h at rt and then evaporated to dryness. Chromatography of the residue (90 mg) on silica (hexane, R_f 0.37) gave adduct **23** (72 mg, 0.16 mmol, 88%) as a white powder, mp 141–142 °C (Found: C 78.80, H 8.70%. $C_{29}H_{38}Si_2$ requires: C 78.66, H 8.65%), which showed δ_H: −0.36 (9H, s, TMS-3(3)), 0.10 (1H, dd, *J*=10.4, 7.0 Hz, H-3(3)), 0.19 (9H, s, TMS-4), 0.34 (1H, d, *J*=9.5 Hz, H-3), 1.03 (1H, ddd, *J*=9.5, 7.0, 4.4 Hz, H-3(1)), 1.48 (1H, d, *J*=6.9 Hz, H-bridge), 1.99 (1H, d, *J*=6.9 Hz, H-bridge), 2.10 (1H, dd, *J*=10.4, 4.4 Hz, H-3(2)), 2.60 (1H, s, H-1), 2.94 (1H, s, H-5), 5.73 (1H, s, H-6), 5.95 (1H, s, H-7), 6.80 (2H, m, Ph), 7.09 (3H, m, Ph), 7.19 (3H, m, Ph), 7.37 (2H, m, Ph); δ_C: −0.2, 0.6, 17.67, 17.73, 19.8, 29.9, 39.9, 45.1, 48.6, 54.0, 58.9, 125.5, 126.1, 127.4, 128.0, 129.3, 131.2, 131.3, 131.9, 140.1, 142.0; υ_{max} ($CHCl_3$, cm^{-1}): 3084 w, 3060 w, 3031 m, 2965 s, 2899 m, 1602 m, 1497 m, 1450 m, 1443 m, 1324 m, 1259 m, 1249 s, 1150 w, 1027 w, 999 m, 912 m, 890 s, 838 s.

*4.7.4. 4,5-Diphenyl-exo-6-(2-phenyl-3-trimethylsilylcyclopropyl)-1-trimethylsilyl-2-oxa-3-azabicyclo[3.1.0]hexene-3 (**24**).* A solution of Et_3N (21 mg, 0.21 mmol, 1.0 mol equiv) in dry ether (0.5 mL) was added dropwise to a stirred mixture of dimer **7** (80 mg, 0.21 mmol) and benzohydroximinoyl chloride (33 mg, 0.21 mmol, 1.0 mol equiv) in dry ether (2 mL) at −15 °C over 1 min. The mixture was stirred for 30 min at −15 °C and 18 h at rt, then quenched with 1 M HCl (1 mL), diluted with water (2 mL) and ether (5 mL). The organic layer was separated and the aqueous layer was extracted with ether (5 mL). The combined organics were washed with water (5 mL), dried and evaporated. Chromatography of the residue (110 mg) on silica (hexane–ether, 10:1) gave adduct **24** (53 mg, 0.11 mmol, 50%, R_f 0.29) and unreacted dimer **7** (15 mg, 0.04 mmol, 19%, R_f 0.82) as colorless oils. Compound **24** (Found M+Na^+: 518.2306. $C_{31}H_{37}NNaOSi_2$ requires: 518.2306) showed δ_H: −0.20 (9H, s, TMS-6(3)), 0.18 (9H, s, TMS-1), 0.43 (1H, dd, *J*=10.6, 6.9 Hz, H-6(3)), 0.89 (1H, d, *J*=10.0 Hz, H-6), 1.52 (1H, ddd, *J*=10.0, 6.9, 4.7 Hz, H-6(1)), 2.54 (1H, dd, *J*=10.6, 4.7 Hz, H-6(2)), 7.17–7.22 (8H, m, Ph), 7.25–7.33 (3H, m, Ph), 7.52–7.54 (4H, m, Ph); δ_C: −1.5, −0.3, 18.3, 19.0, 29.3, 37.2, 50.9, 75.9, 126.2, 127.7, 128.1, 128.2, 128.5, 128.7, 131.0, 131.5, 134.5, 139.4, 163.0; υ_{max} ($CHCl_3$, cm^{-1}): 3087 w, 3063 w, 3032 m, 3010 m, 2958 m, 2901 m, 1954 w, 1888 w, 1810 w, 1602 m, 1591 m, 1579 m, 1549 w, 1498 s, 1445 s, 1422 m, 1353 m, 1323 m, 1310 m, 1260 s, 1251 s, 1180 w, 1094 w, 1025 m, 975 m, 912 m, 845 s.

*4.7.5. 4-(p-Nitrophenyl)-5-phenyl-exo-6-(2-phenyl-3-trimethylsilylcyclopropyl)-1-trimethylsilyl-2-oxa-3-azabicyclo[3.1.0]hexene-3 (**25**).* Compound **25** was prepared in a similar method to the previous experiment from dimer **7** (70 mg, 0.19 mmol), *p*-nitrobenzohydroximinoyl chloride (38 mg, 0.19 mmol, 1.0 mol equiv) in dry ether (2 mL) and Et_3N (19 mg, 0.19 mmol, 1.0 mol equiv) in dry ether (0.5 mL). After 30 min at −15 °C and 40 h at rt subsequent work up and chromatography of the residue (110 mg) on silica (hexane–ether, 10:1) afforded adduct **25** (30 mg, 0.055 mmol, 30%, R_f 0.26) and unreacted dimer **7** (23 mg, 0.06 mmol, 33%, R_f 0.82) as viscous colorless oils. Compound **25** (Found M+Na^+: 563.1929. $C_{31}H_{36}N_2NaO_3Si_2$ requires: 563.2157) showed δ_H: −0.20 (9H, s, TMS-6(3)), 0.18 (9H, s, TMS-1), 0.44 (1H, dd, *J*=10.7, 6.9 Hz, H-6(3)), 0.89 (1H, d, *J*=10.2 Hz, H-6), 1.50 (1H, ddd, *J*=10.2, 6.9, 4.9 Hz, H-6(1)), 2.53 (1H, dd, *J*=10.7, 4.9 Hz, H-6(2)), 7.18–7.25 (6H, m, Ph), 7.34 (2H, t, *J*=7.5 Hz, Ph), 7.50 (2H, d, *J*=7.5 Hz, Ph), 7.65 (2H, d, *J*=8.7 Hz, *p*-NO_2-Ph), 8.01 (2H, d, *J*=8.7 Hz, *p*-NO_2-Ph); δ_C: −1.5, −0.3, 17.9, 19.0, 29.3, 36.7, 49.9, 77.7, 123.5, 126.3, 128.1, 128.2, 128.6, 128.8, 128.9, 131.4, 133.3, 135.0, 138.9, 148.1, 161.2; υ_{max} ($CHCl_3$, cm^{-1}): 2959 m, 1603 m, 1521 s, 1498 m, 1348 s, 1251 m, 914 w, 856 s, 846 s.

4.8. Resolution of *trans*-2,2-dibromo-3-phenylcyclopropanecarboxylic acid (26) with (+)-dehydroabietylamine

*4.8.1. Diastereomeric salt of acid (±)-26 and (+)-dehydroabietylamine (**27**).* A hot solution of (+)-dehydroabietylamine (5.72 g, 20.0 mmol, 0.25 mol equiv) in methanol (100 mL) was added to a hot (60 °C) solution of racemate **26** (25.67 g, 80.2 mmol) in methanol (100 mL). The combined solution was stirred until precipitation of the salt **27** occurred (~10 min), then allowed to slowly cool to rt and left overnight. The product was filtered off from mother liquid, washed with cold methanol (2×20 mL) and dried on air, giving salt **27** (10.17 g, 16.8 mmol, 84%) as a white powder, 62% de, mp 199–201 °C (dec) (Found: C 59.75, H 6.41, N 2.43%. $C_{30}H_{39}Br_2NO_2$ requires: C 59.51, H 6.49, N 2.31%), which showed

υ_{max} (Nujol): 3300–2000 br s, 1640 s, 1585 s, 1560 s, 1510 s, 1470 s, 1370 s, 1325 m, 1310 m, 1270 m, 1245 m, 1220 m, 1180 m, 1163 m, 1142 m, 1090 m, 1055 m, 1040 w, 1030 w, 1010 m, 980 m, 930 w, 890 m, 870 m, 830 s, 790 m, 775 s, 720 s, 702 s cm^{-1}. It was not possible to obtain good NMR data, measure $[\alpha]_D^{25}$ and recrystallize salt **27** due to its low solubility in common solvents.

*4.8.2. (+)-trans-2,2-Dibromo-3-phenylcyclopropanecarboxylic acid [(+)-**26**].* 5% Aq HCl (92 mL) was added to a suspension of salt **27** (8.0 g, 13.2 mmol) in ether (80 mL). The resulting mixture was effectively stirred for 15 min at rt, then diluted with ether (50 mL) and filtered using Buchner funnel. The precipitate was washed with ether (3×30 mL) [after drying on air it gave 4.0 g of pure (+)-dehydroabietylamine hydrochloride (12.4 mmol, 91%), which was further used for recovering of a chiral (+)-amine]. The filtrate was transferred into a separating funnel, the ethereal layer was separated and the water layer was extracted with ether (20 mL). The combined organics phases were washed with water (10 mL) and brine (10 mL), dried and evaporated to give optically active acid (+)-**26** (3.40 g, 11 mmol) as a white powder, mp 120–121 °C, $[\alpha]_D^{25}$ +60 (*c* 1.0, $CHCl_3$), 62% ee. Further enantiomeric enrichment was achieved by slow recrystallization of this sample from benzene–hexane (1:2.5, 130 mL). After 24 h at 5 °C the precipitate of racemate (±)-**26** (1.17 g, 3.7 mmol, 5%) was separated and mother liquid was evaporated to provide (+)-**26** (2.17 g, 6.8 mmol) as a white powder, yield 31% based on recovering of 64% of starting racemate (±)-**26**, mp 117–118 °C, $[\alpha]_D^{25}$ +86 (*c* 1.0, $CHCl_3$), 89% ee. Acid (+)-**26** (Found: C 37.71, H 2.65%. $C_{10}H_8Br_2O_2$ requires: C 37.54, H 2.52%), which showed δ_H: 2.81 (1H, d, *J*=7.8 Hz, H-1), 3.34 (1H, d, *J*=7.8 Hz, H-3), 7.15–7.32 (5H, m, Ph); δ_C: 28.3, 37.0, 41.5, 128.3, 128.6, 128.7, 133.7, 172.4; υ_{max} ($CHCl_3$): 3200–2200 br s, 3060 m, 2591 m, 1950 w, 1708 s, 1603 w, 1496 w, 1442 s, 1311 m, 1170 m, 1082 w, 950 m, 899 m, 862 m, 702 s, 690 s cm^{-1}.

*4.8.3. (-)-trans-2,2-Dibromo-3-phenylcyclopropanecarboxylic acid [(-)-**26**].* 7% Aq $NaHCO_3$ solution (100 mL) was added to the mother liquid (Section 4.8.1), which was evaporated to ca. ~100 mL and diluted with chloroform (70 mL). The resulting mixture was stirred for 20 min, then the water layer was separated and the organic layer was extracted with 5% aq $NaHCO_3$ solution (20 mL). The combined bicarbonate layers were extracted with chloroform (2×30 mL), acidified with 10% aq HCl and subsequent extracted with ether (3×50 mL). The combined ethereal layers were washed with water (50 mL), dried, and evaporated. It gave optically active acid (-)-**26** (18.37 g, 57 mmol) as a white powder, mp 140–142 °C, $[\alpha]_D^{25}$ −10 (*c* 1.0, $CHCl_3$), ~10% ee. Further enantiomeric enrichment was achieved by slow recrystallization of this sample from benzene–hexane (1:2, 150 mL). After 24 h at 5 °C the precipitate of racemate (±)-**26** (15.17 g, 47 mmol, 59%) was separated, mother liquid was evaporated to provide (-)-**26** (3.03 g, 9.5 mmol) as a white powder, yield 34% based on recovering of 64% of starting racemate (±)-**26**, mp 118–119 °C, $[\alpha]_D^{25}$ −88 (*c* 1.0, $CHCl_3$), 91% ee. All analytical and spectral data were identical to those obtained for acid (+)-**26**.

*4.8.4. (+)-trans-2,2-Dibromo-3-phenylcyclopropanecarboxylic acid methyl ester [(+)-**28**].* A mixture of $SOCl_2$ (0.5 mL, 0.81 g, 6.8 mmol) and (+)-**26** (300 mg, 0.94 mmol, 89% ee) was stirred for 15 h at rt and then excess $SOCl_2$ was removed under reduced pressure. The residue was dissolved in dry CH_2Cl_2 (3 mL) and methanol (0.5 mL) was added dropwise followed by cooling to 0 °C and subsequent addition of triethylamine (0.13 mL, 95 mg, 0.94 mmol). The resulting solution was stirred for 2.5 h at rt and diluted with ether (5 mL). The organic layer was extracted with satd aq $NaHCO_3$ (2×5 mL), 10% aq HCl (2×5 mL), washed with water (5 mL), dried, and evaporated. Filtration of the residue (340 mg) on silica (petrol–ether, 5:1, R_f 0.56) afforded methyl ester (+)-**28** (311 mg, 0.93 mmol, 99%) as a white powder, mp 94–96 °C, $[\alpha]_D^{25}$ +90 (*c* 1.0, $CHCl_3$) (Found: C 39.88, H 2.95%. $C_{11}H_{10}Br_2O_2$ requires: C 39.56, H 3.02%), which showed δ_H: 2.89 (1H, d, *J*=8.5 Hz, H-1), 3.43 (1H, d, *J*=8.5 Hz, H-3), 3.84 (3H, s, OMe), 7.24–7.39 (5H, m, Ph); δ_C: 28.6, 37.2, 40.8, 52.8, 128.1, 128.4, 128.6, 133.9, 167.6; υ_{max} ($CHCl_3$): 3090 w, 3065 m, 3033 s, 2955 s, 2855 w, 1741 s, 1605 m, 1585 w, 1499 s, 1440 s, 1406 s, 1319 s, 1290 s, 1270 s, 1199 s, 1171 s, 1105 w, 1081 m, 1051 m, 1013 m, 930 m, 909 m, 857 m, 694 s, 670 s.

*4.8.5. (-)-trans-2-Phenylcyclopropanecarboxylic acid methyl ester [(-)-**29**].* A mixture of (+)-**28** (200 mg, 0.6 mmol) and Bu_3SnH (611 mg, 2.1 mmol, 3.5 mol equiv) in dry benzene (4 mL) was maintained for 6 h at 55 °C overnight at rt. Then solvent was evaporated, the residue (815 mg) was columned on silica (petrol–ether, 10:1, R_f 0.33), giving methyl ester (-)-(1*R*, 2*R*)-**29**[16] (105 mg, 0.6 mmol, 100%) as a colorless liquid, $[\alpha]_D^{25}$ −260 (*c* 1.0, $CHCl_3$), which showed δ_H: 1.33 (1H, ddd, *J*=8.4, 6.5, 4.6 Hz, H-3), 1.60 (1H, ddd, *J*=9.6, 5.1, 4.6 Hz, H-3), 1.90 (1H, ddd, *J*=8.4, 5.1, 4.2 Hz, H-1), 2.53 (1H, ddd, *J*=9.6, 6.5, 4.2 Hz, H-2), 3.71 (3H, s, OMe), 7.08–7.29 (5H, m, Ph); δ_C: 16.9, 23.9, 26.2, 51.8, 126.2, 126.5, 128.5, 140.0, 173.8; υ_{max}: 3445 w, 3095 m, 3070 m, 3037 s, 2960 s, 2938 s, 2864 m, 2100 w, 2040 w, 1960 w, 1895 w, 1840 w, 1733 s, 1610 m, 1500 m, 1464 s, 1445 s, 1405 s, 1348 s, 1331 s, 1275 s, 1210 s, 1182 s, 1125 m, 1085 m, 1062 m, 1010 w, 1000 m, 938 m, 918 m, 852 m, 790 m, 769 s, 732 m, 710 s. Since methyl ester (-)-**29** had (1*R*, 2*R*)-configuration therefore the absolute stereochemistry of (+)-**26** was (1*R*, 3*R*)- and other enantiomer (-)-**26** had (1*S*, 3*S*)-configuration.[21]

*4.8.6. Amide of (+)-trans-2,2-dibromo-3-phenylcyclopropanecarboxylic acid (+)-**26** with L-β-phenylalanine methyl ester [(+)-**30**].* A mixture of $SOCl_2$ (0.5 mL, 0.81 g, 6.8 mmol) and (+)-**26** (200 mg, 0.62 mmol, 89% ee) was stirred for 15 h at rt and then excess $SOCl_2$ was removed in vacuo. The residue was dissolved in dry CH_2Cl_2 (3 mL) and L-β-phenylalanine methyl ester hydrochloride (135 mg, 0.62 mmol, 1.0 mol equiv) was added followed by cooling of the resulting suspension to 0 °C and subsequent addition of triethylamine (0.19 mL, 136 mg, 1.4 mmol, 2.2 mol equiv). The reaction mixture was stirred for 3.5 h at rt and then diluted with ether (2×5 mL). The organic layer was extracted with satd aq $NaHCO_3$ (2×5 mL), 10% aq HCl (2×6 mL), washed with water (5 mL), dried and evaporated. Filtration of the yellow residue (260 mg) on silica (petrol–ether, 1:1, R_f 0.47) afforded amide (+)-**30** (232 mg, 0.48 mmol, 78%) as a yellowish amorphous mass, 89% de by ^1H NMR, $[\alpha]_D^{25}$ +100 (*c* 1.0, $CHCl_3$) (Found: C 50.20, H 4.00, N 2.94%. $C_{20}H_{19}Br_2NO_3$ requires: C 49.92, H 3.98, N 2.91%), which showed δ_H: 2.66 (1H, d, *J*=8.2 Hz, H-1), 3.17 (1H, dd, *J*=13.9, 5.7 Hz, C*H*Ph), 3.25 (1H, dd, *J*=13.9, 6.0 Hz, C*H*Ph), 3.45 (1H, d, *J*=8.2 Hz, H-3), 3.77 (3H, s, OMe), 4.97 (1H, ddd, *J*=7.5, 6.0, 5.8 Hz, C*H*Bn), 6.52 (1H, d, *J*=7.5 Hz, NH), 7.12–7.14 (2H, m, Ph), 7.23–7.39 (8H, m, Ph); δ_C: 29.0, 37.7, 38.3, 39.7, 52.4, 54.0, 127.2, 127.9, 128.3, 128.6, 128.7, 129.2, 134.4, 135.7, 165.0, 171.7; υ_{max}: 3450–3200 br s, 3095 m, 3075 m, 3040 m, 2972 m, 2940 m, 2870 m, 1745 s, 1660 s, 1610 m, 1545 s, 1505 m, 1450 m, 1420 m, 1370 m, 1220 m, 1185 m, 1120 m, 1090 s, 1040 s, 930 w, 865 m, 800 s, 770 s, 710 s. This procedure was also used for the determination of ee for acid (+)-**26** isolated directly from the salt **27** (Section 4.8.2); in this case corresponding amide (+)-**30** showed 62% de by ^1H NMR.

*4.8.7. Amide of (-)-trans-2,2-dibromo-3-phenylcyclopropanecarboxylic acid (-)-**26** with L-β-phenylalanine methyl ester [(+)-**31**].* Compound (+)-**31** was prepared in a method similar to that in the previous experiment from acid (-)-**26** (100 mg, 0.31 mmol, 91% ee), $SOCl_2$ (0.25 mL, 0.4 g, 3.4 mmol), L-β-phenylalanine methyl ester hydrochloride (68 mg, 0.31 mmol, 1.0 mol equiv) and triethylamine

(0.10 mL, 68 mg, 0.7 mmol, 2.2 mol equiv). After filtration on silica (petrol–ether, 1:1, R_f 0.44) the procedure gave amide (+)-**31** (115 mg, 0.24 mmol, 77%) as a yellowish firm film, 91% de by ^{1}H NMR, $[\alpha]_D^{25}$ 24 (*c* 0.62, $CHCl_3$) (Found: C 50.09, H 4.03, N 2.97%. $C_{20}H_{19}Br_2NO_3$ requires: C 49.92, H 3.98, N 2.91%), which showed δ_H 2.72 (1H, d, *J*=8.2 Hz, H-1), 3.19 (2H, d, *J*=5.7 Hz, C*H*$_2$Ph), 3.49 (1H, d, *J*=8.2 Hz, H-3), 3.75 (3H, s, OMe), 5.02 (1H, dd, *J*=8.0, 5.7 Hz, C*H*Bn), 6.55 (1H, d, *J*=8.0 Hz, NH), 7.22–7.34 (10H, m, Ph); δ_C: 29.2, 38.3, 38.7, 39.4, 52.4, 53.8, 127.3, 128.0, 128.4, 128.7, 128.8, 129.5, 134.3, 135.4, 164.7, 171.8; υ_{max}: 3475–3160 br s, 3092 m, 3070 m, 3040 m, 2975 m, 2940 m, 2870 m, 1737 s, 1655 s, 1603 m, 1540 s, 1500 m, 1448 m, 1410 m, 1365 m, 1245 m, 1225 m, 1200 m, 1185 m, 1120 m, 1090 m, 1040 m, 980 m, 925 w, 860 m, 795 w, 762 m, 710 m.

4.9. Generation and ene-reaction of 1-trimethylsilyl-3*S*-phenylcyclopropene (*S*)-2

*4.9.1. (2RS, 3R)-1,1,2-Tribromo-3-phenylcyclopropane [(-)-**4**].* Bromine (0.42 mL, 1.31 g, 8.2 mmol, 1.05 mol equiv) in dry CH_2Cl_2 (30 mL) was added dropwise to a solution of optically active acid (-)-**26** (2.50 g, 7.8 mmol, 91% ee) and red silver (II) oxide (1.27 g, 5.9 mmol, 0.75 mol equiv) in dry CH_2Cl_2 (30 mL) under Ar atmosphere at 0–5 °C over 10 min. After 1 h at 0 °C and 24 h at rt the reaction suspension was filtered through a glass filter and the residue was washed with dichloromethane (30 mL) and hexane (50 mL). The combined organics were concentrated under reduced pressure, diluted with hexane (10 mL) and filtered through a pad of silica (hexane, 3×50 mL). The solvent was removed to give tribromide (-)-**4** (1.22 g, 3.4 mmol, 44%, mixture of isomers, 2*R*:2*S*=6:1 by ^{1}H NMR) as a colorless oil, $[\alpha]_D^{25}$ −6 (*c* 1.7, $CHCl_3$), R_f 0.48 (petrol). All analytical and spectral data were identical to those obtained for racemic tribromide **4**.[7]

*4.9.2. (+)-3,3′-Diphenyl-2,2′-bis-trimethylsilylbicyclopropyl-2-ene [(+)-**7**].* Methyllithium in ether (2.0 mL, 1.85 mmol, 0.92 M, 2.2 mol equiv) was added dropwise to tribromide (-)-**4** (300 mg, 0.84 mmol) in dry ether (10 mL) at −82 to −80 °C over 2 min. The solution was stirred for 5 min at −80 °C and allowed to reach rt (20 min). After a further 30 min at rt the mixture was cooled to −60 °C and chlorotrimethylsilane (0.14 mL, 119 mg, 1.09 mmol, 1.3 mol equiv) was added dropwise. The resulting solution was stirred for 5 min at −60 °C and 1 h at rt, cooled down to −40 °C and quenched with water (2 mL). The organic layer was separated, the aqueous layer was extracted with ether (5 mL). The combined organic layers were washed with water (5 mL), dried, and evaporated. The orange residue (170 mg) was diluted with ether (4 mL) and left overnight under Ar atmosphere. Then the solvent was removed, chromatography on silica (hexane, R_f 0.41) afforded dimer (+)-**7** (14 mg, 0.037 mmol, 9%) as a colorless oil, $[\alpha]_D^{25}$ 149 (*c* 0.47, hexane). The ^{1}H, ^{13}C NMR spectra of (+)-**7** were identical to racemic dimer **7** (Section 4.2.2), however attempts to obtain a good microanalysis for the title compound failed.

*4.9.3. (+)-2-Phenyl-anti-3-(2-phenyl-3-trimethylsilylcyclopropyl)-4-trimethylsilyltricyclo[3.2.1.0^{2,4}]oct-6-ene [(+)-**23**].* The mixture of dimer (+)-**7** (10 mg, 0.027 mmol) and freshly distilled cyclopentadiene (16 mg, 0.24 mmol, 9.0 mol equiv) in benzene (1 mL) was stirred for 24 h at rt, then evaporated under reduced pressure. Chromatography of the residue (15 mg) on silica (petrol, R_f 0.34) gave adduct (+)-**23** (7.5 mg, 0.017 mmol, 64%) as a colorless film, $[\alpha]_D^{25}$ +40 (*c* 0.25, hexane) (Found: C 78.8, H 8.7%. $C_{29}H_{38}Si_2$ requires: C 78.66, H 8.65%). The ^{1}H, ^{13}C NMR spectra were identical to those obtained for racemic **23** (Section 4.7.3).

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References and notes

1. (a) Wiberg, K. B., Part 1 In *The Chemistry of the Cyclopropyl Group*; Rappoport, Z., Ed.; Wiley: New York, NY, 1987; p 1; (b) Salaün, J. *Top. Curr. Chem.* **2000**, *207*, 1–67; (c) Liu, H.-W.; Walsh, C. T. In *The Chemistry of Cyclopropyl Group*; Rappoport, Z., Ed.; Wiley: New York, NY, 1987; Chapter 16, pp 959–1025; (d) Halton, B.; Banwell, M. G. In *The Chemistry of Cyclopropyl Group*; Rappoport, Z., Ed.; Wiley: New York, NY, 1987; Chapter 21, pp 1223–1339; (e) Billups, W. E.; Moorehead, A. W. In *The Chemistry of Cyclopropyl Group*; Rappoport, Z., Ed.; Wiley: New York, NY, 1987; Chapter 24, pp 1533–1574; (f) Rademacher, P. *Chem. Rev.* **2003**, *103*, 933–975.
2. Pietruszka, J. *Chem. Rev.* **2003**, *103*, 1051–1070.
3. de Meijere, A.; Kozhushkov, S. I.; Schill, H. *Chem. Rev.* **2006**, *106*, 4926–4996.
4. See, for example: Verbicky, C. A.; Zercher, C. K. *Tetrahedron Lett.* **2000**, *41*, 8723–8727; Mc Donald, W. S.; Verbicky, C. A.; Zercher, C. K. *J. Org. Chem.* **1997**, *62*, 1215–1222.
5. Breslow, R.; Dowd, P. *J. Am. Chem. Soc.* **1963**, *85*, 2729–2735; Fisher, F.; Applequist, D. E. *J. Org. Chem.* **1965**, *30*, 2089–2090; Weigerd, F. J.; Baird, R. L.; Shapley, J. R. *J. Am. Chem. Soc.* **1970**, *92*, 6630–6635; Eymann, W.; Hanack, M. *Tetrahedron Lett.* **1972**, *41*, 4213–4216; Al Dulayymi, A. R.; Al Dulayymi, J. R.; Baird, M. S.; Koza, G. *Zh. Org. Khim.* **1997**, *33*, 867–885; Lee, G.-A.; Chang, Ch.-Y *J. Org. Chem.* **2004**, *69*, 8949–8951; Garratt, P. J.; Tsotinis, A. *J. Org. Chem.* **1990**, *55*, 84–88; Shi, G.-q.; Huang, X.-h. *Tetrahedron Lett.* **1996**, *37*, 5401–5404; Baird, M. S.; Hussain, H. H.; Clegg, W. *J. Chem. Res.* **1988**, 110–111 (*S*), 1101–1113 (M); Billups, W. E.; Lee, G.-A.; Arney, B. E.; Whitmire, K. H. *J. Am. Chem. Soc.* **1991**, *113*, 7980–7984; Billups, W. E.; Luo, W.; Lee, G.-A.; Chee, J. *J. Org. Chem.* **1996**, *61*, 764–770; Wiberg, K. B.; Artis, D. R.; Bonneville, G. *J. Am. Chem. Soc.* **1991**, *113*, 7969–7979; Lee, G.-A.; Chen, C.-Sh *Tetrahedron Lett.* **1997**, *38*, 8717–8720; Lee, G.-A.; Shiau, Ch.-Sh.; Chen, Ch.-Sh.; Chen, J. *J. Org. Chem.* **1995**, *60*, 3565–3567; Lee, G.-A.; Chang, Ch.-Yi *Tetrahedron Lett.* **1998**, *39*, 3013–3016; Komatsu, K.; Niwa, T.; Akari, H.; Okamoto, K. *J. Chem. Res.* **1985**, 252–253 (*S*), 2847–2881 (*M*); Chen, K. Ch.; Wang, W. Ch.; Chen, M.-Y.; Chen, W.-Ch.; Her, M.-Ch.; Lee, G.-A. *Eur. J. Org. Chem.* **2007**, 953–958; Ashirov, R. V.; Shamov, G. A.; Lodochnikova, O. A.; Litvynov, I. A.; Appolonova, S. A.; Plemenkov, V. V. *J. Org. Chem.* **2008**, *73*, 5985–5988; Matsuura, M.; Saikawa, Y.; Inui, K.; Nakae, K.; Igarashi, M.; Hashimoto, K.; Nakata, M. *Nat. Chem. Biol.* **2009**, *5*, 465–467.
6. (a) Dowd, P.; Gold, A. *Tetrahedron Lett.* **1969**, *2*, 85–86; (b) Deng, Q.; Thomas Iv, B. E.; Houk, K. N.; Dowd, P. *J. Am. Chem. Soc.* **1997**, *119*, 6902–6908; (c) Sakai, S. *J. Phys. Chem. A* **2006**, *110*, 12891–12899.
7. Sheshenev, A. E.; Baird, M. S.; Croft, A. K.; Bolesov, I. G. *Mendeleev Commun.* **2004**, *6*, 299–301; Sheshenev, A. E.; Baird, M. S.; Croft, A. K.; Bolesov, I. G. *Tetrahedron* **2009**, *65*, 10036–10046.
8. Sheshenev, A. E.; Baird, M. S.; Croft, A. K.; Starikova, Z. A.; Shashkov, A. S.; Zhuze, A. L.; Bolesov, I. G. *Tetrahedron Lett.* **2006**, *47*, 2839–2843.
9. Baird, M. S.; Hussain, H. H.; Nethercott, W. *J. Chem. Soc., Perkin Trans. 1* **1986**, 1845–1853.
10. Baird, M. S. *Houben-Weyl, Methods Org. Chem.* **1997**, *E17d*, 182.
11. Baird, M. S.; Dale, C. M.; Al Dulayymi, J. R. *J. Chem. Soc., Perkin Trans. 1* **1993**, 1373–1374.
12. Eisch, J. J.; Foxton, M. W. *J. Org. Chem.* **1971**, *36*, 3520–3526.
13. Backes, J.; Brinker, U. H. *Houben-Weyl, Method Org. Chem.* **1989**, *E19b, Part 1*, 391–510.
14. (a) Bolesov, I. G.; Ignatchenko, A. V.; Zaitseva, L. G.; Plemenkov, V. V. *Modern Probl. Org. Chem.* **1996**, *11*, 74–92; (b) Bolesov, I. G.; Ignatchenko, A. V.; Bovin, N. B.; Prudchenko, I. A.; Surmina, L. S.; Plemenkov, V. V.; Petrovsky, P. V.; Romanov, I. V.; Melnik, I. I. *Zh. Org. Khim.* **1990**, *26*, 102–119; (c) Baird, M. S.; Huber, F. A. M.; Clegg, W. *Tetrahedron* **2001**, *57*, 9849–9858.
15. Baird, M. S.; Licence, P.; Tverezovsky, V. V.; Bolesov, I. G.; Clegg, W. *Tetrahedron* **1999**, *55*, 2773–2784; Riley, ThN; Brier, C. G. *J. Med. Chem.* **1972**, *15*, 1187–1188.
16. (a) Yasui, S. C.; Keiderling, T. A. *J. Am. Chem. Soc.* **1987**, *109*, 2311–2320; (b) Sengmany, S.; Leonel, E.; Paugam, J. P.; Nedelec, J.-Y. *Synthesis* **2002**, 533–537; (c) Güllü, M. *Tetrahedron Lett.* **1999**, *40*, 3225–3228.
17. Liu, K-Ch.; Shelton, B. R.; Howe, R. K. *J. Org. Chem.* **1980**, *45*, 3916–3918.
18. Shipman, M.; Thorpe, H. R.; Clemens, I. R. *Tetrahedron* **1998**, *54*, 14265–14282.
19. Merault, G.; Bourgeois, P.; Dunogues, J.; Duffaut, N. *J. Organomet. Chem.* **1974**, *76*, 17–27.
20. Klein, J.; Brenner, S. *J. Org. Chem.* **1971**, *36*, 1319–1320.
21. Wang, M.-X.; Feng, G.-Q.; Zheng, Q.-Y. *Tetrahedron: Asymmetry* **2004**, *15*, 347–354.