Synthesis of Variously Substituted Spirobenzocyclobutenes

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Abstract: The cobalt(I)-mediated cocyclization between bis(trimethylsilyl)ethyne and monocyclic diyne **8** led to new spirobenzocyclobutene **9**. This quite stable compound was easily transformed into variously substituted spirobenzocyclobutenes which are versatile synthetic intermediates. The full details of the preparation of such compounds are presented.

Key words: cobalt(I), [2+2+2] cycloaddition, spirobenzocyclobutenes, orthoquinodimethanes, [4+2] cyclisation

Substituted benzocyclobutenes have been employed via the intermediacy of *o*-xylylene isomers as versatile building blocks in the construction of complex molecules.[1, 2] In connection with our ongoing program aimed at the rapid construction of the basic skeleton of tetracyclic diterpenes,[3] we were interested in the stereoselective approach of aphidicolin[4] and stemodin **1**,[5] using a common synthetic pathway, based on cobalt-mediated alkyne cyclotrimerizations to give benzocyclobutenes in tandem with intramolecular Diels–Alder cycloadditions involving the resulting *o*-quinodimethane intermediates.[6]

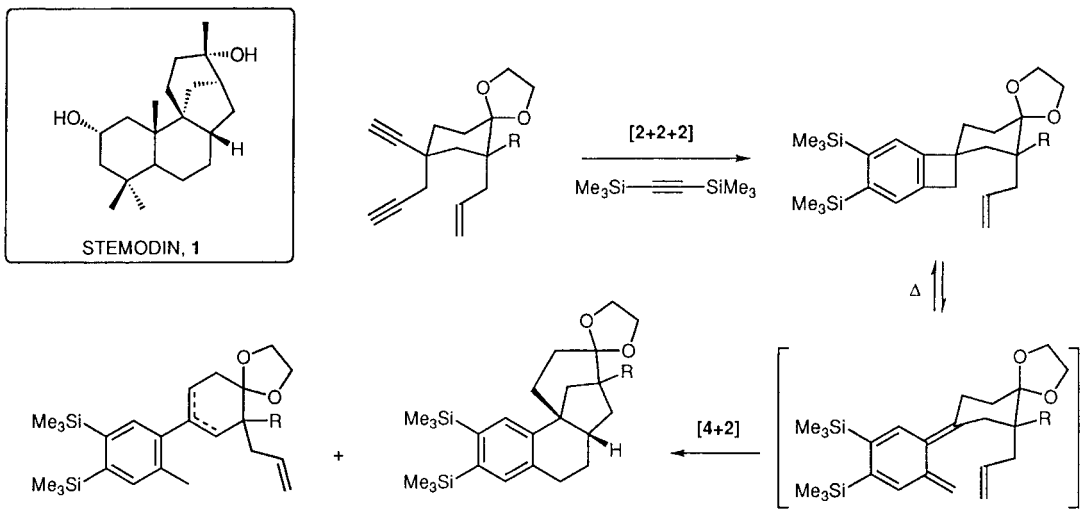
Recently, we have shown[7] that such a tandem strategy allowed the formation of the stemodan skeleton (Scheme 1).

This synthetic sequence deserves various comments: (i) the cobalt-mediated cocyclization between 1,2-bis(trimethylsilyl)ethyne (BTMSE) and the monocyclic diyne led to substituted spirobenzocyclobutenes which have not been reported until now, (ii) when R = allyl, the intramolecular Diels–Alder reaction delivered an equal amount of styrene derivatives resulting from a 1,5-hydrogen shift and the stemodan framework; the ratio 1:1 meaning that the two processes have similar activation energy. To ensure the success of the [4+2] cyclization and to get exclusively the tetracyclic compound, we thought that the dienophile has to be set in the axial position and bear an electron-withdrawing group. Thus, to prepare those variously substituted benzocyclobutenes, we attached a substituent such as an ester group to the cyclohexane which was conceived to facilitate selective introduction of differently susbtituted dienophiles and to render the equatorial/axial ratio more favorable.

Herein we present the full details of the preparation of these substituted spirobenzocyclobutenes which are easy to handle, quite stable compounds and versatile synthetic intermediates.

As a target material, we chose the benzocyclobutene **10**, prepared as depicted in Scheme 2.

Commercially available ethyl 4-oxocyclohexanecarboxylate[8] was quantitatively protected as 1,3-dioxolane **2**. The quaternary center was created by alkylation of the corresponding lithium ester enolate with propargyl bromide leading quantitatively to compound **3**. Reduction of the ester function either with LAH or 2.2 equivalents of DIBAH[9] gave the corresponding alcohol and the following Swern oxidation afforded the aldehyde **5** in 97% yield. It was transformed by chain extension to the alkyne using Corey's procedure.[10] Reaction of **5** with carbon tetrabromide–triphenylphosphine reagent furnished the intermediate dibromoalkene **6** in 97% yield. Reaction of this latter with 3 equivalents of butyllithium and consecutive hydrolysis led to the diyne **7** in 95% yield. Subsequent treatment with formic acid[11] yielded quantitatively the ketone **8**. Exposure of the latter to a catalytic amount of Cp-$Co(CO)_2$ in boiling 1,2-bis(trimethylsilyl)ethyne under ir-

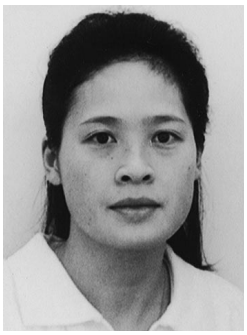


Scheme 1 1 : 1

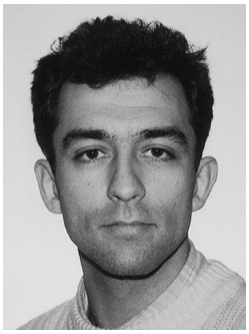
radiation led to the benzocyclobutene **9** in 75% yield. This reaction can be run on gram scale, without affecting the yield of the reaction. Acylation of the preformed lithium enolate of **9** by methyl cyanoformate in diethyl ether[12] in the presence of HMPA at –100°C furnished the β-oxo esters **10** in 79% yield. Not surprisingly with this sterically hindered substrate, only traces of *O*-acylated compound were observed.

Having in hand this key benzocyclobutene, the next steps were devoted to the introduction of various substituents bearing the dienophile moiety (Scheme 3). Alkylation of the potassium enolate of **10** with propargyl bromide pro-

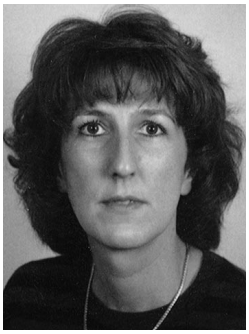
Biographical Sketches



Phannarath Phansavath was born in 1969 in Vientiane, Laos. She studied chemistry at the Pierre & Marie Curie University (Paris VI). She received her Ph. D. in 1997 under the direction of Professor Max Malacria, working on new approaches to taxanes, aphidicolanes and stemodanes skeletons using cobalt-mediated [2+2+2] and [4+2] cycloadditions. She is currently working as a postdoctoral fellow in the group of Professor Carsten Bolm at the Institut für Organische Chemie der RWTH Aachen, Germany.

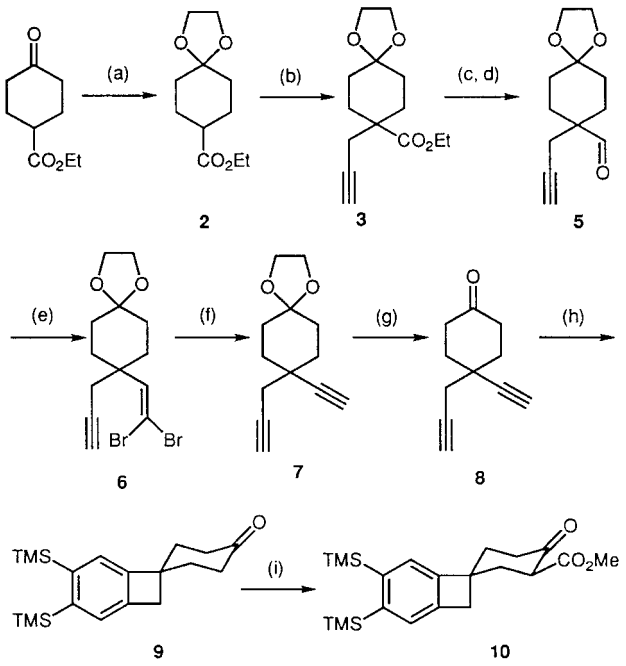


Robert Stammler was born in 1965 and graduated from the Ecole Supérieure de Chimie Industrielle de Lyon (ESCIL) in 1989. He received his Ph. D. degree in 1992 under the supervision of Professor Max Malacria at the University Pierre & Marie Curie (Paris VI), working on new approaches to the basic skeletons of aphidicolanes and stemodanes and on cobalt-mediated Conia-ene type reactions. He is currently working in the Process Department at Rhône-Poulenc Rorer, Vitry sur Seine (France), which he joined in 1992. His interests include new synthetic routes, scale-up and development of new pharmaceutical compounds.



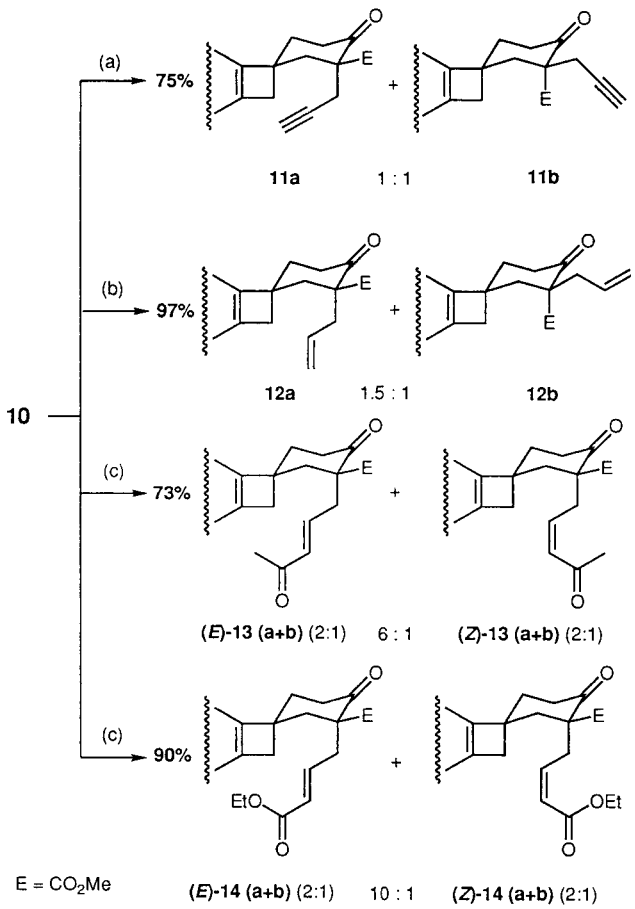
Corinne Aubert was born in 1956 and graduated from the Ecole Nationale Supérieure de Chimie de Strasbourg. She received her Ph. D. degree in 1985 at the University of Paris-Sud, Orsay, under the direction of Dr. J.-F. Biellmann and Dr. J.-P. Bégué. She was appointed by the CNRS in 1985 as Chargée de Recherches in the laboratory of Dr. J.-P. Bégué and worked on fluorine chemistry. After doing postdoctoral research with Professor K. P. C. Vollhardt at the University of California, Berkeley from September 1987 to 1989, she joined the group of Professor Max Malacria at the University Pierre & Marie Curie (Paris VI). Her research interests concern the new developments of transition metal-mediated reactions, the efficient approaches of basic skeletons of polycyclic natural compounds and asymmetric synthesis.

Max Malacria was born in Marseille in 1949. He received his Ph. D. degree in 1974 at the University of Aix-Marseille III under the supervision of Professor Marcel Bertrand. From September 1974 to August 1981, he served as an Assistant and Maître Assistant at the University of Lyon I and worked under the supervision of Professor Jacques Goré. From September 1981 to December 1982, he worked as a postdoctoral fellow with Professor K. Peter C. Vollhardt at the University of California, Berkeley. In 1983, he returned to the University of Lyon I as a Maître de Conférences. In 1988, he was appointed as a Professor at the University Pierre & Marie Curie (Paris VI). In 1991, he was elected as a member of the "Institut Universitaire" de France. His current research interests include the development of new selective and efficient approaches to complex polycyclic molecules, transition metal catalyzed reactions and asymmetric synthesis of natural compounds of biological interests. In 1997, he received the award of the Organic Division of the French Chemical Society.



(a) $HO(CH_2)_2OH$, CSA, toluene, Δ, 20h, quant. (b) 1. LDA, THF, –78 °C; 2. C_3H_3Br quant. (c) LAH, Et_2O, quant. (d) $(COCl)_2$, DMSO, NEt_3, CH_2Cl_2, 97%. (e) CBr_4, PPh_3, CH_2Cl_2, 97%. (f) BuLi, THF, 95%. (g) HCO_2H, $CuSO_4$, pet. ether, quant. (h) $CpCo(CO)_2$, $Me_3SiC{\equiv}CSiMe_3$, hν, Δ, 75%. (i) 1. LDA, Et_2O, –78 °C to 0 °C; 2. $NCCO_2Me$, –100 °C, HMPA, 79%.

Scheme 2

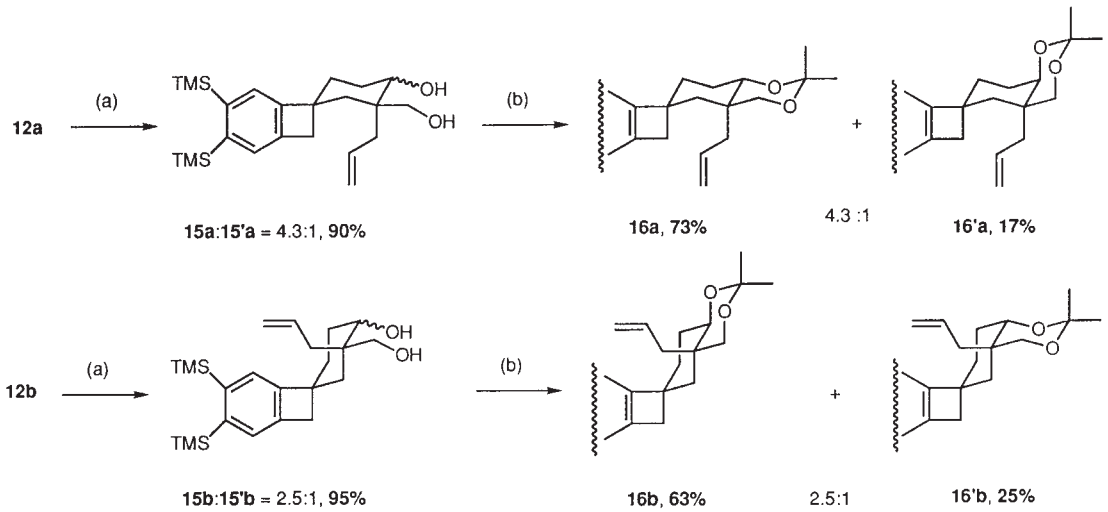


(a) 1. KH THF, 0 °C; 2. C_3H_3Br, HMPA, Δ. (b) THF, 5 mol% $Pd(OAc)_2$, 20 mol% PPh_3, diallyl carbonate. (c)1. NaH, THF, r.t., 45 min; 2. ketone or ester, 5 mol% $Pd(PPh_3)_4$, THF

Scheme 3

vided compound **11** as a 1:1 mixture of diastereomers in 75% yield.[13]

As we have already shown,[7] introduction of the allyl substituent was a little troublesome and eventually Tsuji's procedure[14] was found to be the most reproducible method. Allylation of the β-oxo ester **10** was carried out under neutral conditions by using diallyl carbonate in the presence of a catalytic amount of Pd(0) [generated in situ from 5 mol% of $Pd(OAc)_2$ and 20 mol% of triphenylphosphine] and furnished compound **12** as a 1.5:1 mixture of two diastereomers **12a** and **12b** in 97% yield which were separated by flash column chromatography on silica gel. Their structures were deduced from the assigned stereochemistry of their acetonide derivatives (see Scheme 4).



(a) $LiAlH_4$, Et_2O, 0 °C. (b) 2,2-dimethoxypropane (100 equiv), acetone, cat. PPTS, r.t.

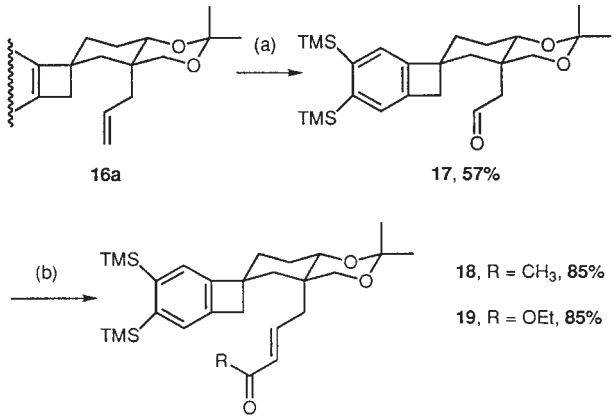
Scheme 4

On the other hand, allylation of **10** with 4-oxopent-2-enyl benzoate[15] was conducted under basic conditions and provided a 6:1 mixture of diastereomers **(*E*)-13** and **(*Z*)-13** in 73% yield. Adducts **(*E*)-13** and **(*Z*)-13** which were separated, consisted of an inseparable 1:2 mixture of diastereomers. Similarly, allylation of **10**, under the same conditions with 4-ethylbenzoyloxycrotonate[15] led in 90% yield to a 10:1 mixture of **(*E*)-14** and **(*Z*)-14** each of which is a 1:2 mixture of diastereomers.

In order to force the dienophile to occupy an axial position, we decided to reduce the β-oxo ester moiety and to transform it into the corresponding acetonides. The conversion of compounds **12a** and **12b** into their acetonides is outlined in Scheme 4. Reduction of the β-oxo esters with LAH in diethyl ether provided a 4.3:1 mixture of diastereomers **15a:15′a** in 90% yield and a 2.5:1 mixture of diols **15b:15′b** in 95% yield. Acid-catalyzed protection of the diols with 2,2-dimethoxypropane in acetone led to the corresponding acetonides **16a:16′a** (4.3:1) and **16b:16′b** (2.5:1) in 90% and 88% yields, respectively. Elucidation of these structures was fully established by decoupling experiments and allowed us to determine the stereochemistry of the previous compounds **15** and **12** (vide infra).

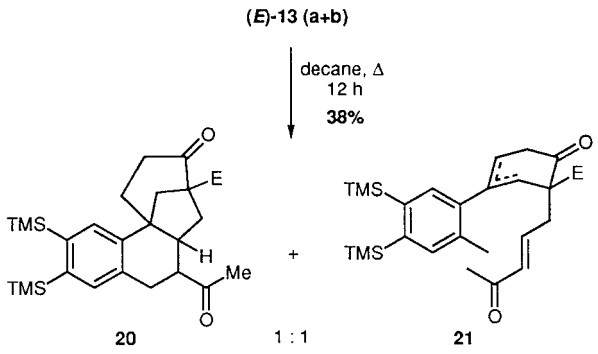
In addition, ozonolysis of compound **16a** furnished the aldehyde **17** in 57% yield. This latter was submitted to the mild alkenation procedure of Masamune et al.[16] by using lithium chloride, DBU and either (2-oxopropyl)phosphonate or triethyl phosphonoacetate in acetonitrile to provide the (*E*)-α,β-unsaturated ketone **18** or ester **19** in 85% yield (Scheme 5).

First studies confirm the validity of our synthetic strategy; for example, substrate **(*E*)-13(a+b)** gave the Diels–Alder product **20** in 19% yield accompanied by the 1,5-hydrogen shift product **21** (19%) (Scheme 6). This preliminary result which was not optimized is very encouraging. We are already engaged in the study aimed at improving the ratio [4+2] / 1,5-hydrogen migration processes.



(a) O_3, CH_2Cl_2, –78 °C; Me_2S, r.t., 30 h.
(b) LiCl, MeCN, $CH_3C(O)CH_2P(O)(OEt)_2$ or $EtOC(O)CH_2P(O)(OEt)_2$, then DBU, THF: MeCN (1:1), r.t., 48 h.

Scheme 5



E=CO_2Me

Scheme 6

In summary, the cobalt(I)-mediated [2+2+2] cycloaddition reaction between bis(trimethylsilyl)ethyne and a monocyclic diyne **8** allowed us to prepare a new spirobenzocyclobutene **9**. We showed that this compound was easy to handle, quite stable and that it was possible to carry out a wide variety of reactions for further transformations. By reduction of the β-oxo ester moiety and its transformation to the corresponding acetonides, we have placed the dienophile in an axial position which in connection with the synthesis of tetracyclic diterpenes in the family of stemodane augurs well for the success of the intramolecular [4+2] cyclization.

^{1}H NMR and ^{13}C NMR spectra were measured on 200 MHz Bruker AC 200, 400 MHz JEOL 65X 400 and Bruker ARX 400 spectrometers. Chemical shifts are reported in ppm referenced to the residual proton resonances of the solvents. IR spectra were recorded by using a Perkin Elmer 1420 spectrometer. Mass spectra (MS) were obtained on GCMS Hewlett-Packard HP 5971 apparatus. TLC was performed on Merck silica gel 60 F 254. Silica gel Merck Geduran SI (40–63 μm) was used for column chromatography using Still method.[17] PE and EE are petroleum ether and Et_2O. The melting points reported are uncorrected and the compounds are not recrystallized.

8-Ethoxycarbonyl-1,4-dioxaspiro[4.5]decane (2):
A solution of ethyl 4-oxocyclohexanecarboxylate (8.0 g, 47.0 mmol), ethylene glycol (13.0 mL, 235 mmol) and (±)-10-camphorsulfonic acid (102 mg, 0.5 mmol) in toluene (150 mL) was refluxed with a Dean–Stark apparatus for 20 h. The solution was cooled and toluene was evaporated. The residue was diluted with Et_2O (200 mL) and neutralized with sat. $NaHCO_3$ (50 mL). The organic layer was washed with brine (3 × 50 mL), dried (Na_2SO_4), filtered and concentrated. The residue was purified by flash chromatography (PE/EE = 80/20) to give **2** (10.1 g, 47.0 mmol, 100%).
^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.12 (q, J = 7.0 Hz, 2H), 3.93 (s, 4H), 2.33 (tt, J = 10.3, 4,0 Hz, 1H), 1.92 (m, 2H), 1.78 (m, 4H), 1.54 (td, J = 11.8, 4.5 Hz, 2H), 1.24 (t, J = 7.0 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ = 175.0, 108.0, 64.3 (2C), 60.2, 41.6, 33.8 (2C), 26.3 (2C), 14.2.
IR (neat) ν = 2960, 1730, 1190, 1110 cm^{-1}.

8-Ethoxycarbonyl-8-(prop-2-ynyl)-1,4-dioxaspiro[4.5]decane (3):
At –78°C, a solution of **2** (5.8 g, 27.0 mmol) in THF (30 mL) was added dropwise to a solution of LDA (4.4 mL, 31.4 mmol) in THF (30 mL). The mixture was slowly warmed to 0 °C, then cooled to –78 °C and a solution of propargyl bromide (2.3 mL, 30.5 mmol) in THF (15 mL) was added dropwise over 15 min. The mixture was stirred at –78°C for 1h, warmed to 0°C and diluted with Et_2O (60 mL),

The organic layer was washed with sat. NH_4Cl (2 × 30 mL) and brine (2 × 30 mL), dried (Na_2SO_4), filtered and concentrated. The residue was purified by flash chromatography (PE/EE = 70/30) affording **3** (6.8 g, 27.0 mmol, 100%) as a colorless oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.19 (q, J = 7.0 Hz, 2H), 3.93 (s, 4H), 2.42 (d, J = 2.6 Hz, 2H), 2.05 (t, J = 2.6 Hz, 1H), 2.18 (m, 2H), 1.66 (m, 6H), 1.27 (t, J = 7.0 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ = 174.7, 108.2, 79.8, 71.2, 64.3 (2C), 60.7, 45.7, 31.8 (2C), 30.6 (2C), 28.9, 14.3.
IR (neat) ν = 3300, 2960, 2120, 1730, 1190 cm^{-1}.

8-Hydroxymethyl-8-(prop-2-ynyl)-1,4-dioxaspiro[4.5]decane (4):
At 0°C, a solution of 3 (5.4 g, 21 mmol) in Et_2O (70 mL) was added dropwise to a suspension of $LiAlH_4$ (0.42 g, 11.0 mmol) in Et_2O (70 mL). After being stirred at 0°C for 5 min, the mixture was diluted with CH_2Cl_2 (140 mL) and hydrolyzed with sat. Na_2SO_4 until a white suspension is formed. The mixture was filtered on Celite and concentrated. Recrystallization (Et_2O) of the crude residue furnished **4** (4.5 g, 21.0 mmol, 100%) as a white solid, mp 67°C.
^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.94 (s, 4H), 3.58 (s, 2H), 2.29 (d, J = 2.6 Hz, 2H), 2.02 (t, J = 2.6 Hz, 1H), 1.61 (m, 8H).
^{13}C NMR (100 MHz, $CDCl_3$) δ = 108.7, 81.6, 70.7, 67.4, 64.2 (2C), 36.9, 30.4 (2C), 29.2 (2C), 24.2.
IR ($CHCl_3$) ν = 3400, 3300, 2960, 2120, 1110 cm^{-1}.
Anal. Calcd for $C_{12}H_{18}O_3$: C, 68.54 ; H, 8.63. Found : C, 68.43 ; H, 8.67.

8-Formyl-8-(prop-2-ynyl)-1,4-dioxaspiro[4.5]decane (5):
A solution of DMSO (2.7 mL, 38.0 mmol) in CH_2Cl_2 (8 mL) was added dropwise at –78 °C to a solution of oxalyl chloride (1.6 mL, 18.6 mmol) in CH_2Cl_2 (40 mL). After 5 min, a solution of **4** (3.4 g, 16.0 mmol) in CH_2Cl_2 (16 mL) was added dropwise. After stirring at –78 °C for 15 min, Et_3N (11.0 mL, 80.0 mmol) was added quickly. The mixture was warmed to r.t. (45 min), diluted with Et_2O (250 mL), washed with sat. NH_4Cl (2 × 100 mL), brine (2 × 100 mL), dried (Na_2SO_4), filtered and concentrated. Purification by flash chromatography (PE/EE = 50/50) furnished **5** (3.2 g, 15.5 mmol, 97%) as a colorless oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.51 (s, 1H), 3.87 (s, 4H), 2.29 (d, J = 2.6 Hz, 2H), 1.98 (t, J = 2.6 Hz, 1H), 2.01 (m, 2H), 1.64 (m, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ = 204.6, 107.9, 79.0, 71.5, 64.3 (2C), 47.7, 31.0 (2C), 27.8 (2C), 25.0.
IR (neat) ν = 3300, 2960, 2720, 2120, 1730, 1100 cm^{-1}.

8-(2,2-Dibromoethenyl)-8-(prop-2-ynyl)-1,4-dioxaspiro[4.5]decane (6):
At 0 °C, a solution of CBr_4 (14.6 g, 44.2 mmol) in CH_2Cl_2 (40 mL) was added dropwise to a solution of PPh_3 (23.2 g, 88.4 mmol) in CH_2Cl_2 (40 mL). After being stirred at 0°C for 30 min, a solution of **5** (4.6 g, 22.1 mmol) in CH_2Cl_2 (20 mL) was added dropwise. After the mixture was stirred for 2.5 h at 0°C, it was diluted with pentane (400 mL), filtered on Celite and concentrated. The residue was purified by flash chromatography (PE/EE = 80/20) to yield **6** (7.8 g, 21.4 mmol, 97%): white solid, mp 70 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.56 (s, 1H), 3.94 (s, 4H), 2.50 (d, J = 2.6 Hz, 2H), 2.01 (t, J = 2.6 Hz, 1H), 2.16 (m, 2H), 1.64 (m, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ = 141.8, 107.9, 87.6, 80.5, 70.7, 64.2 (2C), 41.8, 32.4 (2C), 31.3 (2C), 27.7.
IR ($CHCl_3$) ν = 3300, 3040, 2960, 2120, 1640, 1600, 1100 cm^{-1}.

8-Ethynyl-8-(prop-2-ynyl)-1,4-dioxaspiro[4.5]decane (7):
To a cooled (–78 °C) THF (70 mL) solution of dibromoalkene **6** (4.23 g, 11.6 mmol) was added dropwise a solution of BuLi (1.5 M in hexane, 31 mL, 46.5 mmol). After stirring at –78 °C for 15 min, the mixture was allowed to warm to 0 °C and partitioned between H_2O (150 mL) and hexane (150 mL). The organic layer was washed with sat. NH_4Cl (2 × 50 mL), brine (3 × 40 mL), dried (Na_2SO_4), filtered and concentrated. Flash chromatography (PE/EE = 60/40) gave **7** (2.25 g, 11.0 mmol, 95%) as a white solid, mp 39 °C (PE/EE = 60/40).
^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.92 (m, 4H), 2.38 (d, J = 2.6 Hz, 2H), 2.21 (s, 1H), 2.09 (t, J = 2.6 Hz, 1H), 1.94 (m, 2H), 1.83 (m, 2H), 1.65 (m, 4H).
^{13}C NMR (100 MHz, $CDCl_3$) δ = 108.2, 87.1, 80.4, 70.9 (2C), 64.2 (2C), 35.4, 34.0 (2C), 31.8, 31.6 (2C).
IR ($CHCl_3$) ν = 3300, 3280, 2960, 2120, 1100 cm^{-1}.

4-Ethynyl-4-(prop-2-ynyl)cyclohexanone (8):
A solution of **7** (1.7 g, 8.3 mmol) and formic acid (12.0 mL, 40 equiv) dried over anhyd $CuSO_4$ in PE (6 mL) was stirred at r.t. for 20 min. The mixture was diluted with hexane (100 mL), neutralized with K_2CO_3 (5 g) and with sat. $NaHCO_3$ (2 × 50 mL). The organic layer was washed with brine (2 × 20 mL), dried (Na_2SO_4), filtered and concentrated. The crude residue was purified by flash chromatography (PE/EE = 70/30) to yield **8** (1.2 g, 7.5 mmol, 90%) as a white solid, mp 57 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.78 (td, J = 14.7, 5.9 Hz, 2H), 2.52 (d, J = 2.6 Hz, 2H), 2.36 (s, 1H), 2.35 (m, 2H), 2.15 (m, 2H), 2.13 (t, J = 2.6 Hz, 1H), 1.87 (td, J = 13.6, 4.2 Hz, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ = 210.5, 86.0, 79.8, 72.3, 71.7, 38.3 (2C), 36.2 (2C), 35.5, 31.6.
IR ($CHCl_3$) ν = 3280, 3260, 2940, 2120, 1730 cm^{-1}.

3,4-Trimethylsilylspiro[benzocyclobutene-1,1′-cyclohexan-4′-one] (9):
The reaction was carried out under Ar in a flame-dried flask, washed with hexamethyldisilazane and all the solutions were degassed by three freeze-pump-thaw cycles. A solution of diyne **8** (1.1 g, 6.8 mmol) and $CpCo(CO)_2$ (85 μL, 0.7 mmol) in degassed BTMSE (22 mL) and xylenes (22 mL) was added dropwise over 15 min to a boiling degassed solution of BTMSE (30 mL) and $CpCo(CO)_2$ (85 μL, 0.7 mmol). Light from a projector lamp (ELW, 300W, 60% of its power) was directed at the mixture during the addition. After the mixture was refluxed and irradiated for 3h, the solvent was removed by vacuum transfer. The crude residue was purified by flash chromatography (PE/EE = 90/10) to give the benzocyclobutene **9** (1.7 g, 5.1 mmol, 75%) as a white solid, mp 147 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.52 (s, 1H), 7.50 (s, 1H), 3.13 (s, 2H), 2.63–2.46 (m, 4H), 2.24–2.14 (m, 4H), 0.38 (s, 9H), 0.37 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ = 211.4, 151.2, 145.9, 144.7, 141.4, 130.2, 127.1, 49.6, 41.8, 39.9 (2C), 35.8 (2C), 2.3 (6C).
IR ($CHCl_3$) ν = 2970, 1710, 1240, 840 cm^{-1}.
Anal. Calcd for $C_{19}H_{30}OSi_2$: C, 69.02; H, 9.15. Found: C, 69.38; H, 9.31.
MS (m/z) = 330, 315, 299, 131, 73, 59.

Compound (10):
At –78 °C, a solution of **9** (2.3 g, 6.9 mmol) in Et_2O (9 mL) was added dropwise to a solution of LDA (3.7 mL, 6.9 mmol) in Et_2O (18 mL). The mixture was warmed to 0 °C and stirred at 0 °C for 1h. After being cooled to –100 °C, HMPA (0.74 mL, 6.9 mmol) and methyl cyanoformate (0.65 mL, 8.2 mmol) were added. After being stirred for 5 min at –100 °C, the mixture was hydrolyzed at –l00 °C with sat. NH_4Cl and extracted with Et_2O. The organic layer was washed with brine, dried (Na_2SO_4), filtered and concentrated. The residue was purified by flash chromatography (PE/EE = 90/10) affording a mixture of the β-oxo ester **10** and its enol form **10′** (2.0 g, 5.2 mmol, 79%) as a white solid, mp 136 °C.

10: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.46 (s, 1H), 7.33 (s, 1H), 3.79 (d, J = 7.7 Hz, 1H), 3.72 (s, 3H), 3.03 (d, J = 13.7 Hz, 1H), 2.98 (d, J = 13.7 Hz, 1H), 2.60–1.96 (m, 6H), 0.35 (s, 9H), 0.34 (s, 9H).
10′: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 12.21 (s, 1H), 7.45 (s, 1H), 7.33 (s, 1H), 3.77 (s, 3H), 3.00 (s, 2H), 2.59–1.97 (m, 6H), 0.34 (s, 9H), 0.33 (s, 9H).
(10+10′) ^{13}C NMR (100 MHz, $CDCl_3$) δ = 205.5, 172.8, 171.7, 152.0, 145.4, 144.5, 141.6, 129.9, 126.9, 96.7, 55.6, 51.3, 48.0, 42.7, 32.8, 30.8, 27.9, 2.3.
IR ($CHCl_3$) ν = 2980, 1730, 1660, 1620, 1250, 840, 760 cm^{-1}.

Compound (11):
At 0°C, a THF (2.0 mL) solution of benzocyclobutene **10** (0.77 g, 2.0 mmol) was added dropwise to a suspension of KH (0.22 g, 2.2 mmol) in THF (2.0 mL). After being stirred at r.t. for 30 min, the reaction was cooled at 0°C, then HMPA (1.4 mL, 8.0 mmol) and propargyl bromide (0.29 mL, 2.6 mmol) were successively added. The mixture was refluxed for 30 min, cooled to r.t., washed with sat. NH_4Cl and extracted with Et_2O. The organic layer was washed with brine, dried (Na_2SO_4), filtered and concentrated. The crude residue was purified by flash chromatography (pentane/Et_2O= 90/10) to furnish **11** (0.64 g, 1.5 mmol, 75%) as a 1:1 mixture of two diastereomers **11a** and **11b.**
11a: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.46 (s, 1H), 7.34 (s, 1H), 3.78 (s, 3H), 3.19 (d, *J* = 13.7 Hz, 1H), 3.08 (d, *J* = 13.7 Hz, 1H), 2.88–2.55 (m, 6H), 2.34 (d, *J* = 13.7 Hz, 2H), 2.04 (t, *J* = 2.7 Hz, 1H), 0.37 (s, 9H), 0.36 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ = 205.9, 171.9, 150.4, 146.2, 144.9, 141.4, 130.0, 125.7, 79.6, 71.2, 58.4, 52.7, 48.6, 43.5, 41.4, 38.8, 36.8, 25.4, 2.3 (6C).
11b: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.47 (s, 1H), 7.40 (s, 1H), 3.71 (s, 3H), 3.14 (d, *J* = 13.7 Hz, 1H), 3.04 (d, *J* = 13.7 Hz, 1H), 2.93–2.58 (m, 6H), 2.38 (d, *J* = 13.7 Hz, 2H), 2.04 (t, *J* = 2.7 Hz, 1H), 0.37 (s, 9H), 0.36 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ = 206.0, 171.8, 150.4, 145.9, 144.5, 140.8, 130.1, 128.1, 79.7, 71.5, 58.8, 52.7, 49.0, 43.4, 42.9, 39.0, 36.9, 25.4, 2.5 (6C).
(11a+11b) IR ($CHCl_3$) ν = 2940, 2170, 1730, 1450, 1260, 840, 690 cm^{-1}.

Compound (12):
At r.t. under Ar, $Pd(OAc)_2$ (27 mg, 0.12 mmol) was added in one portion to a solution of triphenylphosphine (133 mg, 0.5 mmol) in THF (5 mL). After stirring for 5 min, a solution of **10** (0.94 g, 2.4 mmol) in THF (25 mL) and diallyl carbonate (0.7 mL, 4.8 mmol) were added. The mixture was stirred for 20 min and then concentrated. The crude residue was purified by flash chromatography (PE/EE = 95/5) to afford **12** as a 1.5:1 mixture of diastereomers **12a** (0.61 g, 1.4 mmol, 59%) and **12b** (0.4 g, 0.9 mmol, 38%).
12a: white solid mp 93 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.47 (s, 1H), 7.39 (s, 1H), 5.82 (ddt, *J* = 15.9, 11.0, 7.1 Hz, 1H), 5.04 (d, *J* = 11.0 Hz, 1H), 5.03 (d, *J* = 15.9 Hz, 1H), 3.66 (s, 3H), 3.08 (d, *J* = 13.7 Hz, 1H), 3.00 (d, *J* = 13.7 Hz, 1H), 2.95 (td, *J* = 13.7, 5.5 Hz, 1H), 2.80 (dd, *J* = 14.3, 2.7 Hz, 1H), 2.58 (dd, *J* = 13.7, 8.0 Hz, 1H), 2.54 (dt, *J* = 13.7, 3.7 Hz, 1H), 2.40 (dd, *J* = 13.7, 7.0 Hz, 1H), 2.13 (d, *J* = 14.1 Hz, 1H), 2.11 (m, 2H), 0.37 (s, 9H), 0.36 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ = 207.4, 172.5, 150.5, 145.5, 144.2, 140.6, 133.6, 129.9, 128.0, 118.4, 59.5, 52.0, 49.2, 44.4, 42.7, 40.1, 39.4, 37.2, 2.6 (3C), 2.4 (3C).
12b: colorless oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.46 (s, 1H), 7.33 (s, 1H), 5.81 (ddt, *J* = 15.9, 11.0, 7.1 Hz, 1H), 5.04 (d, *J* = 11.0 Hz, 1H), 5.03 (d, *J* = 15.9 Hz, 1H), 3.73 (s, 3H), 3.30 (d, *J* = 13.7 Hz, 1H), 3.04 (d, *J* = 13.7 Hz, 1H), 2.85 (td, *J* = 13.7, 6.1 Hz, 1H), 2.72 (dd, *J* = 14.3, 2.7 Hz, 1H), 2.52 (dt, *J* = 13.7, 3.8 Hz, 1H), 2.60 (dd, *J* = 13.7, 8.2 Hz, 1H), 2.35 (dd, *J* = 13.7, 6.5 Hz, 1H), 2.19–2.11 (m, 3H), 0.36 (s, 9H), 0.35 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ = 207.5, 172.5, 150.6, 145.5, 144.2, 140.6, 133.6, 129.9, 128.0, 118.4, 59.5, 52.0, 49.2, 44.4, 42.7, 40.1, 39.4, 37.2, 2.6 (3C), 2.4 (3C).
(12a+12b): IR ($CHCl_3$) ν = 3080, 2960, 1740, 1720, 1640, 1460, 1250, 850 cm^{-1}.
Anal. Calcd. for $C_{24}H_{36}O_3Si_2$: C, 67.24; H, 8.46. Found: C, 67.38; H, 8.65.

Compounds 13 and 14; General procedure:
A solution of benzocyclobutene **10** (0.4 g, 1.0 mmol) in THF (2 mL) was added dropwise to a suspension of NaH (60% in oil, 40 mg, 1.0 mmol) in THF (2 mL). After being stirred for 45 min at r.t., the resulting mixture was added dropwise to a solution of freshly prepared tetrakis(triphenylphosphine)palladium(0) (58 mg, 0.05 mmol) and either 4-oxopent-2-enyl benzoate (204 mg, 1.0 mmol) or 4-ethylbenzoyloxycrotonate (234 mg, 1.0 mmol) in THF (4 mL). The mixture was stirred for an additional 15 min and partitioned between sat. NH_4Cl (15 mL) and Et_2O (10 mL). The organic layer was washed with brine (2 × 15 mL), dried ($MgSO_4$), filtered and concentrated.

Compound 13: Purification by flash chromatography (PE/EE = 60/40) furnished the α,β-unsaturated ketones **13** (73%) as a mixture of 4 diastereomers: (*Z*)-**13** (0.05 g, 0.1 mmol, 10%), which is a mixture of 1:2 diastereomers (*Z*)-**13a** and (*Z*)-**13b** and (*E*)-**13** (0.30 g, 0.63 mmol, 63%), which is a mixture of 1:2 diastereomers (*E*)-**13a** and (*E*)-**13b.**
(*Z*)-**13a**: ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.40 (s, 1H), 7.33 (s, 1H), 6.18–5.92 (m, 2H), 3.60 (s, 3H), 3.29–2.46 (m, 10H), 2.11 (s, 3H), 0.31 (s, 9H), 0.30 (s, 9H).
^{13}C NMR (50 MHz, $CDCl_3$) δ = 207.7, 199.1, 172.8, 150.5, 145.9, 144.4, 142.6, 140.9, 130.1, 128.5, 127.9, 59.4, 52.4, 49.1, 44.8, 42.9, 39.3, 37.2, 34.9, 31.0, 2.4 (6C).
(*Z*)-**13b**: ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.40 (s, 1H), 7.27 (s, 1H), 6.18–5.92 (m, 2H), 3.69 (s, 3H), 3.29–2.46 (m, 10H), 2.14 (s, 3H), 0.30 (s, 9H), 0.28 (s, 9H).
^{13}C NMR (50 MHz, $CDCl_3$) δ = 207.7, 199.0, 172.8, 150.5, 146.0, 144.7, 142.3, 141.6, 130.1, 128.6, 126.3, 58.9, 52.5, 48.9, 44.5, 41.3, 39.2, 37.2, 31.5, 29.8, 2.4 (6C).
(*Z*)-13(a+b): IR (CH_2Cl_2) ν = 3020, 2980, 1710, 1610, 1420, 1250, 840 cm^{-1}.
(*E*)-13a: ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.47 (s, 1H), 7.37 (s, 1H), 6.83–6.74 (m, 1H), 5.99 (d, *J* = 16.2 Hz, 1H), 3.65 (s, 3H), 3.28–2.07 (m, 10H), 2.21 (s, 3H), 0.36 (s, 9H), 0.35 (s, 9H).
^{13}C NMR (50 MHz, $CDCl_3$) δ = 207.2, 198.5, 172.2, 150.2, 145.9, 144.4, 142.9, 140.6, 134.5, 130.1, 128.0, 59.5, 52.4, 49.2, 45.2, 42.8, 39.5, 38.8, 37.3, 26.5, 2.4 (6C).
(*E*)-13b: ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.46 (s, 1H), 7.33 (s, 1H), 6.83–6.74 (m, 1H), 6.01 (d, *J* = 15.7 Hz, 1H), 3.73 (s, 3H), 3.28–2.07 (m, 10H), 2.21 (s, 3H), 0.35 (s, 9H), 0.34 (s, 9H).
^{13}C NMR (50 MHz, $CDCl_3$) δ = 207.2, 198.5, 172.2, 150.2, 146.3, 145.0, 142.7, 141.4, 134.5, 130.1, 126.2, 59.2, 52.6, 48.8, 44.6, 41.2, 39.0, 38.6, 37.3, 26.6, 2.4 (6C).
(*E*)-13(a+b): IR (CH_2Cl_2) ν = 3040, 2950, 1720, 1710, 1670, 1620, 1430, 1250, 850 cm [1].
Anal. Calcd. for $C_{26}H_{38}O_4Si_2$: C, 66.34; H, 8.13. Found: C, 66.41 ; H, 8.26.

Compound 14: Purification by flash chromatography (PE/EE = 80/20) furnished the α,β-unsaturated esters **14** (90%) as a mixture of 4 diastereomers: (*Z*)-**14** (0.04 g, 0.08 mmol, 8%), which is a mixture of l:2 diastereomers (*Z*)-**14a** and (*Z*)-**14b** and (*E*)-**14** (0.41 g, 0.82 mmol, 82%), which is a mixture of 1:2 diastereomers (*E*)-**14a** and (*E*)-**14b.**
(*Z*)-**14a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.45 (s, 1H), 7.38 (s, 1H), 6.23–6.16 (m, 1H), 5.82 (d, *J* = 11.7 Hz, 1H), 4.17–4.12 (m, 2H), 3.65 (s, 3H), 3.27–2.07 (m, 10H), 1.38–1.24 (m, 3H), 0.36 (s, 9H), 0.35 (s, 9H).
^{13}C NMR (50 MHz, $CDCl_3$) δ = 207.5, 172.6, 166.1, 150.4, 145.8, 144.4, 140.8, 130.0, 128.4, 126.2, 121.8, 59.9, 59.2, 52.3, 49.1, 44.6, 42.9, 39.2, 37.1, 34.3, 14.2, 2.4 (6C).
(*Z*)-14b: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.44 (s, 1H), 7.32 (s, 1H), 6.23–6.16 (m, 1H), 5.82 (d, *J* = 11.7 Hz, 1H), 4.17–4.12 (m, 2H), 3.73 (s, 3H), 3.27–2.07 (m, 10H), 1.38–1.24 (m, 3H), 0.35 (s, 9H), 0.33 (s, 9H).
^{13}C NMR (50 MHz, $CDCl_3$) δ = 207.3, 172.6, 166.1, 150.4, 145.8, 144.4, 141.4, 130.0, 128.4, 126.2, 121.8, 59.9, 58.7, 52.5, 48.8, 44.2, 41.3, 38.9, 37.1, 34.4, 14.4, 2.5 (6C).
(*Z*)-**14(a+b)**: IR (CH_2Cl_2) ν =2950, 1720, 1640, 1430, 1180, 840 cm^{-1}.
(*E*)-**14a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.49 (s, 1H), 7.40 (s, 1H), 6.96–6.88 (m, 1H), 5.85 (d, *J* = 16.9 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.71 (s, 3H), 3.33–2.09 (m, 10H), 1.30 (t, *J* = 7.1 Hz, 3H), 0.39 (s, 9H), 0.38 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 206.7, 172.2, 165.9, 150.5, 145.9, 144.4, 143.5, 140.8, 130.2, 128.2, 125.0, 60.4, 59.3, 52.5, 49.3, 44.8, 42.9, 39.5, 38.4, 37.4, 14.4, 2.5 (6C).
(*E*)-**14b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.48 (s, 1H), 7.36 (s, 1H), 6.96–6.88 (m, 1H), 5.85 (d, *J* = 16.9 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.78 (s, 3H), 3.33–2.09 (m, 10H), 1.30 (t, *J* = 7.1 Hz, 3H), 0.38 (s, 9H), 0.37 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ = 206.7, 172.2, 165.9, 150.6, 146.2, 145.0, 143.4, 141.6, 129.8, 128.6, 126.3, 60.4, 59.1, 52.7, 48.9, 44.4, 41.4, 39.0, 37.4 (2C), 14.4, 2.5 (6C).
(*E*)-**14(a+b)**: IR (CH_2Cl_2) ν = 2950, 1720, 1650, 1430, 1200, 850 cm^{-1}.
Anal. Calcd. for $C_{27}H_{40}O_5Si_2$: C, 64.76; H, 8.05. Found: C, 64.54 ; H, 8.37.

Diols (15); General Procedure:
The benzocyclobutenes **12a** and **12b** were reduced following the procedure described above for the preparation of compound **4**. The diol **15a** was obtained as a 4.3:1 mixture of 2 diastereomers **15a** and **15′a** (90%).
15a: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.41 (s, 1H), 7.30 (s, 1H), 5.97–5.90 (m, 1H), 5.26–5.12 (m, 2H), 3.89–3.85 (m, 1H), 3.64 (m, 1H), 3.46 (m, 1H), 3.25 (m, 1H), 3.04 (m, 1H), 2.65 (m, 1H), 2.30 (m, lH), 1.84–1.33 (m, 8H), 0.35 (s, 9H), 0.34 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.9, 145.4, 144.4, 142.0, 134.8, 129.9, 125.9, 118.2, 78.3, 71.6, 48.4, 43.7, 42.4, 36.7, 35.0, 29.7, 28.3, 2.4 (6C).
15′a: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.46 (s, 1H), 7.42 (s, 1H), 5.97–5.90 (m, 1H), 5.26–5.12 (m, 2H), 3.89–3.85 (m, 1H), 3.64 (m, 1H), 3.46 (m, 1H), 3.25 (m, 1H), 3.04 (m, 1H), 2.65 (m, 1H), 2.30 (m, 1H), 1.84–1.33 (m, 8H), 0.36 (s, 9H), 0.35 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.2, 144.9, 144.1, 141.9, 134.1, 129.9, 125.5, 118.1, 78.3, 67.4, 48.9, 44.0, 42.1, 36.7, 35.0, 30.3, 29.3, 2.4 (6C).
(15+15′)a: IR (CH_2Cl_2) ν = 3620, 3520, 3080, 2960, 1650, 1250, 850 cm^{-1}.
The diol **15b** was obtained as a 2.5:1 mixture of 2 diastereomers **15b** and **15′b** (95%).
15b: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.56 (s, 1H), 7.44 (s, 1H), 5.81–5.71 (m, 1H), 5.19–5.03 (m, 2H), 3.91–3.88 (m, 1H), 3.64 (m, 1H), 3.46 (m, 1H), 3.04–1.31 (m, 10H), 0.38 (s, 9H), 0.37 (s, 9H).
15′b: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.44 (s, 1H), 7.34 (s, 1H), 5.98–5.92 (m, 1H), 5.19–5.03 (m, 2H), 4.26 (m, 1H), 3.64 (m, 1H), 3.48 (m, 1H), 3.04–1.31 (m, 10H), 0.38 (s, 9H), 0.37 (s, 9H).
(15+15′)b: IR (CH_2Cl_2) ν = 3620, 3520, 3080, 2960, 1650, 1250, 850 cm^{-1}.

Acetonides (16); General Procedure:
To a solution of **15a** (0.51 g, 1.3 mmol) in acetone (7.8 mL, 63.4 mmol) and 2,2-dimethoxypropane (9.3 mL, 127 mmol) was added pyridinium *p*-toluenesulfonate (16 mg, 0.06 mmol) at r.t. After stirring for 10 min, acetone was evaporated and the crude residue was partitioned between sat. $NaHCO_3$ and Et_2O. The organic layer was washed with brine, dried (Na_2SO_4), filtered and concentrated. Purification by flash chromatography (PE/EE = 95/5) led to the acetonides **16a.** They were obtained as a 4.3:1 mixture of 2 diastereomers **16a** and **16′a** (90%). **16a** (0.42 g, 0.95 mmol, 73%): white solid, mp 140°C.
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.43 (s, 1H), 7.33 (s, 1H), 5.88–5.80 (m, 1H), 5.25 (d, *J* = 16.9 Hz, 1H), 5.16 (d, *J* = 10.1 Hz, 1H), 3.85 (dd, *J* = 11.5, 3.8 Hz, 1H), 3.66 (d, *J* = 11.0 Hz, 1H), 3.44 (d, *J* = 11.0 Hz, 1H), 3.28 (d, *J* = 13.7 Hz, 1H), 3.07 (d, *J* = 13.7 Hz, 1H), 2.82 (dd, *J* = 14.0, 7.5 Hz, 1H), 2.25 (dd, *J* = 14.0, 6.2 Hz, 1H), 1.97–1,57 (m, 4H), 1.79 (d, *J* = 14.1 Hz, 1H), 1.54 (s, 3H), 1.49 (s, 3H), 1.39 (d, *J* = 14.1 Hz, 1H), 0.37 (s, 9H), 0.36 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.2, 145.7, 144.7, 142.3, 134.7, 130.3, 126.1, 118.7, 99.7, 76.6, 68.8, 48.6, 45.0, 37.8, 36.6, 36.2, 30.2, 29.5, 25.2, 19.5, 2.7 (6C).
16′a (0.098 g, 0.22 mmol, 17%): white foam.
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.42 (s, 1H), 7.39 (s, 1H), 5.78–5.69 (m, 1H), 5.10 (d, *J* = 17.3 Hz, 1H), 5.08 (d, *J* = 9.9 Hz, 1H), 3.84 (br s, 1H), 3.74 (d, *J* = 12.1 Hz, 1H), 3.28 (d, *J* = 12.1 Hz, 1H), 3.16 (d, *J* = 13.2 Hz, 1H), 3.01 (d, *J* = 13.2 Hz, 1H), 2.58 (d, *J* = 14.0 Hz, 1H), 2.32 (dd, *J* = 14.3, 7.7 Hz, 1H), 2.18 (m, 1H), 1.98 (dd, *J* = 14.3, 6.8 Hz, 1H), 1.83 (m, 1H), 1.68 (m, 1H), 1.57 (m, 1H), 1.51 (s, 3H), 1.47 (s, 3H), 1.44 (m, 1H), 0.35 (s, 18H).
^{13}C NMR (100 MHz, $CDCl_3$) δ = 154.1, 144.9, 144.4, 142.1, 132.5, 129.8, 126.3, 118.5, 97.9, 70.3, 68.5, 49.2, 43.9, 38.3, 34.9, 34.0, 29.9, 29.8, 25.4, 19.0, 2.4 (6C).
(16+16′)a: IR ($CHCl_3$) ν = 3080, 2980, 1640, 1250, 11 10, 850 cm^{-1}.
Acetonides **16b** were obtained from diols **15b** (0.44 g, 1.09 mmol) as a 2.5:1 mixture of diastereomers **16b** and **16′b** (88%). **16b** (0.36 g, 0.81 mmol, 63%): white solid, mp 143 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.62 (s, 1H), 7.43 (s, 1H), 5.64–5.57 (m, 1H), 5.07 (d, *J* = 17.0 Hz, 1H), 5.02 (d, *J* = 10.1 Hz, 1H), 3.84 (m, 1H), 3.63 (d, *J* = 11.0 Hz, 1H), 3.42 (d, *J* = 11.0 Hz, 1H), 2.95 (d, *J* = 13.8 Hz, 1H), 2.89 (d, *J* = 13.8 Hz, 1H), 2.87 (dd, *J* = 13.7, 9.2 Hz, 1H), 2.71 (dd, *J* = 13.7, 5.7 Hz, 1H), 2.05–1.58 (m, 6H), 1.52 (s, 3H), 1.51 (s, 3H), 0.38 (s, 9H), 0.37 (s, 9H)
^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.1, 144.8, 144.1, 141.8, 134.4, 129.9, 129.4, 118.7, 99.6, 76.7, 68.7, 48.9, 44.7, 37.6, 37.4, 35.8, 30.0, 28.9, 25.4, 19.4, 2.4 (6C).
16′b (0.14 g, 0.32 mmol, 25%): white solid, mp 114 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.55 (s, 1H), 7.45 (s, 1H), 5.70–5.60 (m, 1H), 5.02 (d, *J* = 17.0 Hz, 1H), 5.00 (d, *J* = 6.6 Hz, 1H), 3.93 (br s, 1H), 3.79 (dd, *J* = 13.7, 9.2 Hz, 1H), 3.26 (d, *J* = 11.8 Hz, 1H), 2.97 (s, 2H), 2.53–1.52 (m, 8H), 1.49 (s, 3H), 1.47 (s, 3H), 0.38 (s, 9H), 0.36 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.1, 144.6, 143.7, 142.3, 132.7, 130.1, 129.0, 118.3, 97.8, 70.1, 68.5, 49.7, 45.0, 38.1, 35.6, 34.9, 29.7, 29.6, 26.2, 19.1, 2.4 (6C).
Anal. Calcd. for $C_{26}H_{42}O_2Si_2$: C, 70.53 ; H, 9.56. Found: C, 70.58; H, 9.61.

Compound (17):
At –78 °C, a stream of ozone was bubbled through a solution of **16a** (0.49 g, 1.10 mmol) in CH_2Cl_2 (17 mL) until a persistent blue color was perceived, indicating an excess of ozone. The excess ozone was then chased away by bubbling N_2 through the solution for 20 min, to give a colorless mixture. Dimethyl sulfide (2.4 mL, 33 mmol) was added dropwise and the mixture was allowed to warm to r.t. After stirring for 30 h, the reaction was concentrated. The crude residue was purified by flash chromatography (PE/EE = 80/20) to afford aldehyde **17** (0.28 g, 0.63 mmol, 57%).
^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.07 (d, *J* = 1.7 Hz, 1H), 7.47 (s, 1H), 7.39 (s, 1H), 3.98 (d, *J* = 1.6 Hz, 1H), 3.85 (t, *J* = 7.8 Hz, 1H), 3.72 (d, *J* = 1.6 Hz, 1H), 3.29 (d, *J* = 16.5 Hz, 1H), 3.19 (d, *J* = 13.6 Hz, 1H), 3.11 (d, *J* = 13.6 Hz, 1H), 2.58 (dd, *J* = 16.5, 1.7 Hz, 1H), 1.99 (m, 2H), 2.05 (d, *J* = 14.2 Hz, 1H), 1.72 (m, 2H), 1.64 (d, *J* = 14.2 Hz, 1H), 1.58 (s, 3H), 1.52 (s, 3H), 0.41 (s, 18H).
^{13}C NMR (100 MHz, $CDCl_3$) δ = 203.0, 152.5, 145.8, 144.7, 141.9, 130.2, 126.0, 100.0, 76.3, 69.2, 48.2, 45.0, 41.4, 39.9, 38.4, 37.6, 35.6, 25.3, 19.3, 2.6 (6C).
IR ($CHCl_3$) ν = 2940, 2720, 1720, 1450, 1250, 850 cm^{-1}.

Compounds 18 and 19; General Procedure:
To a solution of lithium chloride (31 mg, 0.74 mmol) [dried 2h at 100°C under vacuum 1 mmHg] in MeCN (6 mL) was added dropwise a solution of either diethyl (2-oxopropyl)phosphonate (122 mg, 0.74 mmol) or triethyl phosphonoacetate (166 mg, 0.74 mmol) in MeCN (3 mL). To this resulting mixture, were added dropwise DBU (92 µL, 0.61 mmol) and a solution of aldehyde **17** (0.273 g, 0.61 mmol) in a 1:1 THF:MeCN mixture (6 mL). After being stirred for 48 h at r.t., the mixture was hydrolyzed with sat. NH_4Cl and extracted with Et_2O. The organic layer was washed with brine, dried ($MgSO_4$), filtered and concentrated. Purification of the crude residue

by flash chromatography (PE/EE = 70/30) furnished either **18** (0.25 g, 0.52 mmol, 85%) or **19** (0.27 g, 0.52 mmol, 85%).

18: white foam.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.45 (s, 1H), 7.34 (s, 1H), 6.90 (m, 1H), 6.31 (d, *J* = 16.3 Hz, 1H), 3.89 (dd, *J* = 10.7, 4.6 Hz, 1H), 3.61 (d, *J* = 11. 1 Hz, 1H), 3.54 (d, *J* = 11.1 Hz, 1H), 3.21 (d, *J* = 13.7 Hz, 1H), 3. 11 (d, *J* = 13.7 Hz, 1H), 3.01 (m, 1H), 2.43 (m, 1H), 2.25 (s, 3H), 1.95–l.59 (m, 6H), 1.55 (s, 3H), 1.49 (s, 3H), 0.38 (s, 9H), 0.37 (s, 9H).

^{3}C NMR (100 MHz, $CDCl_3$) δ = 195.6, 153.0, 145.6, 144.3, 143.1, 141.9, 134. 1, 130.3, 125.8, 99.4, 76.0, 68.4, 48.2, 44.8, 38.0, 36.4, 35.7, 29.9, 28.6, 27.0, 25.0, 19. 1, 2.4 (3C), 2.3 (3C).

IR ($CHCl_3$) ν = 2940, 1690, 1670, 1620, 1240, 840 cm^{-1}.

Anal. Calcd. for $C_{28}H_{44}O_3Si_2$: C, 69.37; H, 9.49. Found: C, 69.49; H, 9.21.

19: white foam.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.47 (s, 1H), 7.36 (s, 1H), 7.01 (m, 1H), 6.06 (d, *J* = 15.7 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.89 (dd, *J* = l0.6, 4.5 Hz, 1H), 3.64 (d, *J* = 11.7 Hz, 1H), 3.53 (d, *J* = 11.7 Hz, 1H), 3.26 (d, *J* = 13.7 Hz, 1H), 3. 12 (d, *J* = 13.7 Hz, 1H), 3.01 (m, 1H), 2.41 (m, 1H), 2.00–1.66 (m, 6H), 1.55 (s, 3H), 1.49 (s, 3H), 1.30 (s, 3H), 0.40 (s, 9H), 0.39 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.3, 152.7, 145.9, 145.6, 144.7, 141.9, 130.2, 126.0, 124.9, 99.8, 76.3, 68.7, 60.3, 48.3, 44.9, 38.8, 36.6, 35.8, 29.9, 28.4, 25. 1, 19.3, 14.4, 2.5 (6C).

IR ($CHCl_3$) ν – 2940, 1710, 1640, 1240, 840 cm^{-1}.

Compound (20):

A degassed solution of benzocyclobutenes (*E*)-**13(a+b)** (0.220 g, 0.47 mmol) in decane (10 mL) was heated at reflux for 12 h. The solvent was removed by vacuum transfer and the crude mixture was purified by flash chromatography (PE/EE = 80/20) to afford 20 (43 mg, 0.09 mmol, 19%) and **21** (41 mg, 0.09 mmol, 19%).

20:

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.53 (s, 1H), 7.41 (s, 1H), 3.73 (s, 3H), 2.93–1.72 (m, 12H), 2.29 (s, 3H), 0.36 (s, 9H), 0.35 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 210.0, 207.3, 171.5, 144.7, 144.0, 139.6, 135.7, 135.6, 133.9, 64.2, 54.4, 52.2, 45.9, 45.4, 43.0, 41.0, 38.7, 35.4, 34.0, 29.8, 1.9, 1.8.

IR ($CHCl_3$) ν = 2970, 1740, 1710, 1550, 1420, 1250, 850, 750 cm^{-1}.

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