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Synthesis of new terpene derivatives via ruthenium catalysis: rearrangement of silylated enynes derived from terpenoids

Jérôme Le Nôtre, Ana Acosta Martinez, Pierre H. Dixneuf and Christian Bruneau*

Institut de Chimie, UMR 6509, Organométalliques et Catalyse, Université de Rennes 1 Campus de Beaulieu-35042 Rennes Cedex, France

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Abstract—Enyne rearrangement of silylated modified terpenoids has been used as the key step for the synthesis of new terpenes and terpenoids. The catalytic system generated in situ from $[RuCl_2(p\text{-cymene})]_2$, 1,3-bis(mesityl)imidazolinium chloride and cesium carbonate is able to perform the transformation of silylated 1,7-enynes into cyclic siloxanes. Selective cleavage of the silicon–carbon and silicon–oxygen bonds by simple reactions has been performed to afford new terpenes and terpenoids by formal addition of a C5 unit.

1. Introduction

The intramolecular cyclic rearrangement of enynes represents a powerful tool for the formation of carbon–carbon bond in synthetic organic chemistry.[1–3] This catalytic reaction using mostly ruthenium precursors tolerates a large number of functionalities[4] and allows the synthesis of natural compounds or analogues.[5] It has been shown that alkylidene ruthenium catalysts[6] or in situ generated catalytic systems based on ruthenium species[7] were able to transform Si–O containing enynes into metathesis type silylated vinylcycloalkenes. These vinylallylsilanes present a great interest in synthesis due to the presence of the siloxane group which react under selected conditions to provide 3-vinyltetrahydrofurans,[8] allylic alcohols[9] or allylic diols.[6,10] The temporary introduction of the Si–O group makes possible the easy modification of chemical structures which would required multi-step organic transformations.

On the other hand, terpenes and terpenoids represent an important class of natural products possessing interesting organoleptic properties.[11] Their simple chemical modifications via organic reactions[12] or metal-catalysed reactions[13] such as hydrogenation,[13c] hydroformylation[13d] or diene metathesis[14] allow the formation of new molecules with unprecedented properties in the field of flavours or fragrances. We have recently reported that the intramolecular rearrangement of 1,6-enynes to produce five membered heterocyclic derivatives could efficiently be catalysed by a simple three component system generated in situ from $[RuCl_2(p\text{-cymene})]_2$, an imidazolium or imidazolinium salt and bases[7,15] and that this catalytic system could be used to prepare spiro compounds bearing a five membered dihydrofuran ring from terpenoids containing a carbonyl group.[16]

We now report the use of the same in situ prepared catalysts to produce new terpenes and terpenoids by formal addition of a C5 unit to natural compounds via sequential reactions including a cyclic rearrangement of Si–O containing enynes, as exemplified from menthone in Scheme 1.

We show that starting from the natural carbonyl-containing terpenoids **1**, the corresponding enynes **2** can easily be synthesised in two steps by addition of lithium acetylide and reaction of allyldimethylchlorosilane with the intermediate propargylic alcohols. The cyclic rearrangement of the silylated enynes **2** to give the corresponding cyclic allylsilanes **3** occurs in the presence of the in situ generated catalytic system based on the ruthenium dimer $[RuCl_2(p\text{-cymene})]_2$, 1,3-bis(mesityl)imidazolinium chloride and cesium carbonate. Different selective transformations of the siloxane function open the route to the novel terpenes **4** and **5** and terpenoids **6**.

2. Results and discussion

Silylated enynes were prepared in two steps starting from the natural terpenoids: (−)-menthone **7**, (−)-carvone **8**, (+)-pulegone **9**, citral (*cis*+*trans*) **10** and (−)-myrtenal **11**, and isolated in good yields. Treatment of acetylene in tetrahydrofuran (−78°C) by *n*-butyllithium gave the corresponding monoacetylide as a white suspension. Addition of the natural terpenoid bearing a ketone or an aldehyde function led to the corresponding propargylic

Keywords: homogeneous catalysis; enyne rearrangement; ruthenium catalyst; terpenoids; cyclic siloxanes.

* Corresponding author. Tel.: +33-2-23-23-62-83; fax: +33-2-23-23-69-39; e-mail: christian.bruneau@univ-rennes1.fr

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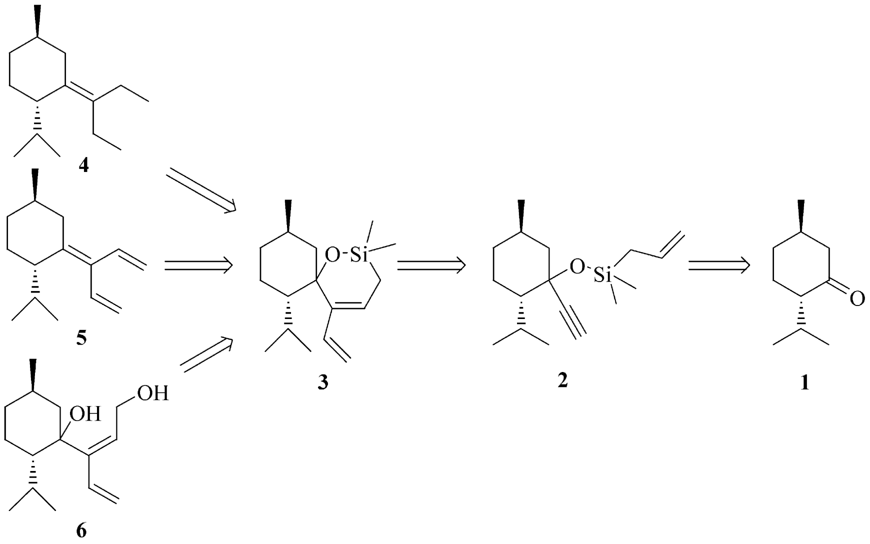


Scheme 1. Retrosynthetic strategy.

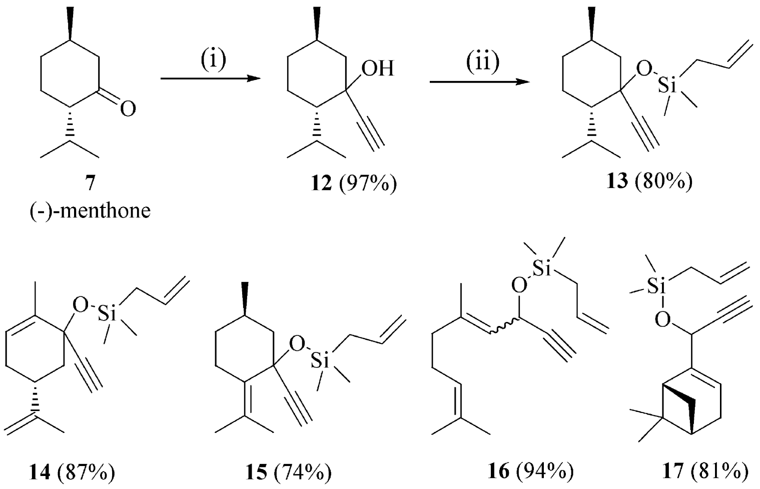
alcohol which was obtained in very good yield (91–97%) after quenching with an acidic aqueous solution. As indicated by ^{13}C NMR, there was no stereocontrol in this addition and the two stereoisomers were formed in various proportions depending on the initial carbonyl compound and the precise reaction conditions. Subsequent treatment of these propargylic alcohols with allylchlorodimethylsilane in the presence of triethylamine and a catalytic amount of 4-dimethylaminopyridine at room temperature led to the formation of the corresponding silylated 1,7-enynes **13–17** in good yields (74–94% based on the alcohol) (Scheme 2).

Starting from the enynes **13–17**, the cyclic rearrangement was performed by using the in situ generated ruthenium catalytic system recently developed in the laboratory,[7,15,16] which is based on commercially available and air stable materials. Indeed, the in situ generated catalytic system was prepared from the dimer [$RuCl_2$(*p*-cymene)]$_2$, 1,3-bis(mesityl)imidazolinium chloride and cesium carbonate in the molar ratio 1:2:4. The cyclisation of the silylated 1,7-enynes **13–15**, **17** was achieved within 16 h at 80°C in toluene by using 1.25–2.5 mol% of the ruthenium complex (Scheme 3).

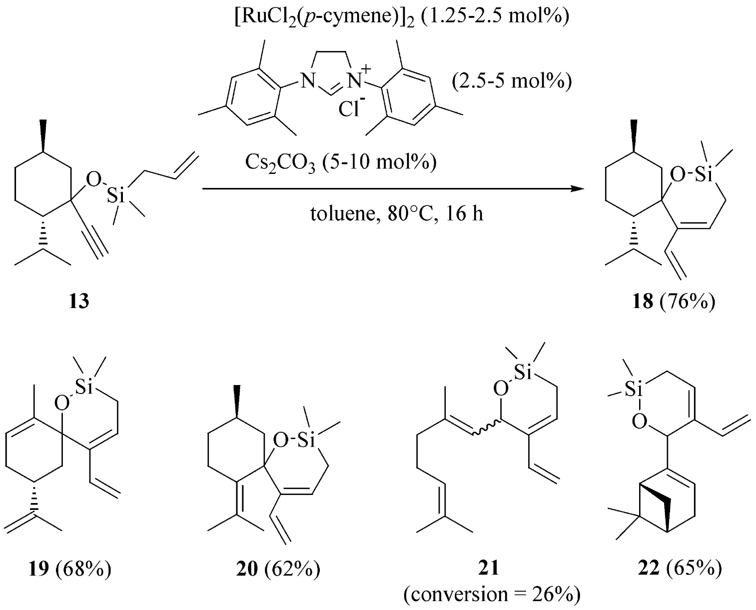
The corresponding six membered rings **18–20**, **22** were isolated in 76, 68, 62, 65% yield, respectively, after distillation under vacuum rather than flash chromatography to avoid degradation of the products on silica gel. Under similar conditions, the conversion of the silylated enyne **16** arising from citral was very slow (26%) and the use of 5 mol% of [$RuCl_2$(*p*-cymene)]$_2$, a higher temperature reaction (120°C) or a longer reaction time did not improve the formation of the cyclic product. Moreover, the high structural similarity of the starting enyne **16** and the cyclic siloxane **21** did not allow their separation by chromatography or distillation. The cyclic compound **21** was yet observed by GC–MS.

In addition to their conjugated diene structure, which has already been used to perform [2+4] cycloaddition reactions,[7] the cyclic siloxane compounds present interesting properties due to the specific reactivity of the Si–O-allyl group to afford desilylated products.

For instance, under Tamao oxidative conditions,[17] cyclic allylsiloxanes are known to give allylic diols.[6,10] Applied to



Scheme 2. Synthesis of the silylated enynes **13–17**. *Reagents and conditions*: (i) acetylene, *n*-BuLi, THF, −78°C to rt then H_2O; (ii) allylchlorodimethylsilane, DMAP, Et_3N, CH_2Cl_2, rt.

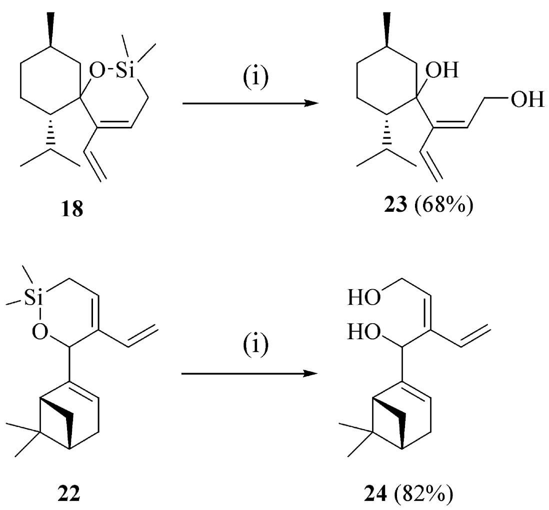


Scheme 3. Enyne cycloisomerisation.

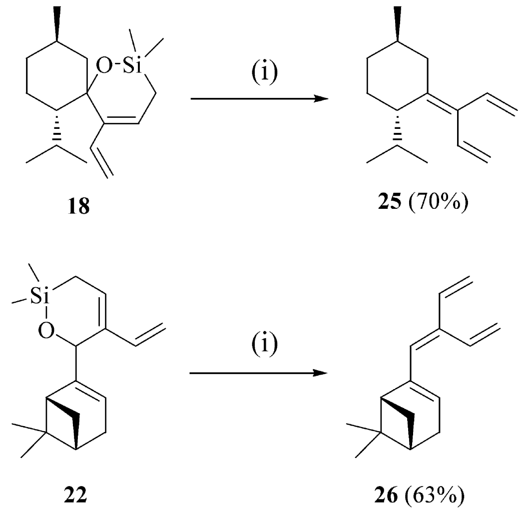
the cyclic siloxanes that we have obtained from natural terpenoids, this reaction can lead to the higher class of terpenoids containing two additional allylic alcohol functionalities. Thus, the cyclic allylsilanes **18** and **22** were oxidized with an excess of hydrogen peroxide in a THF/MeOH mixture in the presence of potassium fluoride and potassium hydrogen carbonate at 40°C for 24 h (Scheme 4) and the diols **23** and **24** were isolated in 68 and 82% yield, respectively. These three step transformations of **7** and **11** into new terpenoids with formal addition of a C5 unit represent a modifications which would be difficult to perform in a simple manner.

The cyclic siloxanes **18** and **22** were reacted in CH_2Cl_2 at −78°C with an excess of tetrabutylammonium fluoride in solution in THF. After one night stirring at room temperature, the polyenes **25** and **26** were isolated in 70 and 63% yield, respectively (Scheme 5). Under these conditions desilylation and complete selective dehydration took place to form the trienes **25** and **26**, which are representatives of a new class of nonnatural terpenes bearing a highly unsaturated C_5H_6 group connected to the terpene structure through its central carbon atom via an alkylidene double bond.

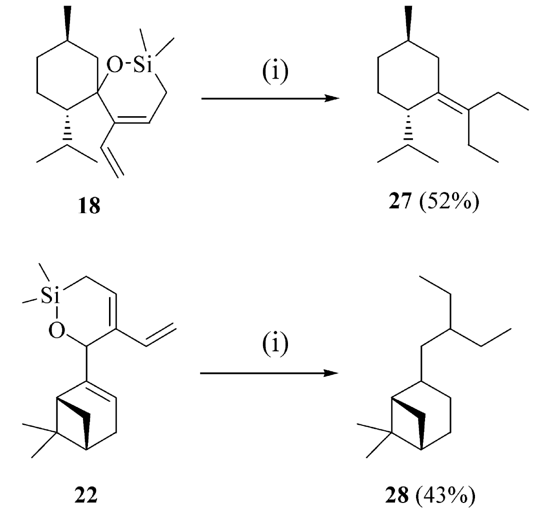
The hydrolysis/hydrogenation of **18** and **22** with palladium on charcoal under an atmosphere of hydrogen was investigated and led to desilylated compounds. The treatment of the cyclic siloxane **18** with 10 wt% of Pd/C under an atmosphere of hydrogen at room temperature in dichloromethane afforded the compound **27** in a moderated yield (52%). The overall reaction leads to formal hydrogenation of the terminal double bonds of **25** (Scheme 6). Under the same conditions, the cyclic siloxane **22** led to the very volatile saturated product **28** isolated in only 43% yield. These new terpenes **27** and **28** correspond to the partially or completely hydrogenated analogs of compounds **25** and **26**, respectively.



Scheme 4. Oxidative cleavage with hydrogen peroxide. *Reagents and conditions*: (i) KF, $KHCO_3$, H_2O_2, THF/MeOH, 40°C, 24 h.



Scheme 5. Cleavage of the siloxane function by fluorine anion. *Reagents and conditions*: (i) NBu_4F 1.0 M in THF, CH_2Cl_2, −78°C to rt, 16 h.



Scheme 6. Cleavage of the siloxane function by hydrogenation. *Reagents and conditions*: (i) Pd/C, H_2 (1 atm), CH_2Cl_2, rt, 16 h.

3. Conclusion

We have shown that the synthesis of new nonnatural terpenes and terpenoids was possible from natural terpenoids by using, as the key step, the formation of cyclic siloxanes via a catalytic enyne rearrangement. This selective catalytic transformation represents another example of the usefulness of this cyclisation reaction with atom economy. The easily available catalytic system generated in situ from $[RuCl_2(p\text{-cymene})]_2$ as a ruthenium source, 1,3-bis(mesityl)imidazolinium chloride and cesium carbonate was used to carry out the cycloisomerisation of silylated 1,7-enynes. The specific reactivity of cyclic allylic siloxane makes possible the preparation of new terpenic diols via controlled oxidation with hydrogen peroxide and new terpenes via desilylation under neutral conditions with a fluoride salt or under reducing conditions with hydrogen in the presence of a catalytic amount of palladium on charcoal.

4. Experimental

4.1. General experimental procedures

All experiments except the hydrogenation reactions were carried out in Schlenk tubes under an inert atmosphere of nitrogen. The solvents were dried and distilled prior to use. ^{1}H and ^{13}C NMR were recorded with a Bruker AC 200 MHz spectrometer and GC–MS were performed with a CE Instrument GC 8000 Top (capillary column OV1, 25 m×0.35 mm, 0.1–0.15 μm) chromatograph linked to a Automass II Finnigan MAT (70 eV) apparatus. The HRMS analyses were carried out with a Varian MAT311 spectrometer.

4.2. Preparation of silylated enynes

4.2.1. Allyl-(1-ethynyl-2(*S*)-isopropyl-5(*R*)-methylcyclohexyloxy)-dimethylsilane (13). Acetylene (450 mL, 20.1 mmol) and 15 mL of dry tetrahydrofuran were cooled down to −78°C, then *n*-butyllithium (5.0 mL, 8.1 mmol) and after 30 min at −78°C, (−)-menthone **7** (1.0 g, 6.7 mmol) were slowly added. After 1 h stirring at −78°C the reaction mixture was treated with 1N HCl to give, after column chromatography on silica gel (eluent: heptane/diethyl ether, 15:1), the propargylic alcohol (1.2 g, 97%). Subsequently, this alcohol (1.2 g, 6.5 mmol) was treated with allylchlorodimethylsilane (1.1 mL, 7.2 mmol), DMAP (80 mg, 0.65 mmol) and triethylamine (1.3 g, 13.0 mmol) at room temperature in dry dichloromethane (20 mL) for 16 h. The column was eluted with a heptane/diethyl ether (30:1) mixture to give the silylated enyne **13** (1.45 g, 80%) as a colourless oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.16–0.23 (m, 6H, $Si(CH_3)_2$), 0.78–1.01 (m, 9H, 3×CH_3), 1.10–1.41 (m, 4H, $CH(CH_3)CH_2CH_2$), 1.60–1.73 (m, 5H, $SiCH_2$-$CH{=}CH_2$, $CH(CH_3)CH_2C$(quat.)), 1.90–1.99 (dm, 1H, $^3J_{HH}$=13.8 Hz, $CHCH(CH_3)_2$), 2.11–2.28 (m, 1H, $CHCH(CH_3)_2$), 2.49 (s, 1H, $C{\equiv}CH$), 4.80–4.90 (m, 2H, $SiCH_2CH{=}CH_2$), 5.70–5.92 (m, 1H, $SiCH_2CH{=}CH_2$). ^{13}C NMR (50 MHz, $CDCl_3$): δ −0.93, −0.76, 17.9, 21.9, 23.4, 25.9, 26.3, 30.3, 34.7, 52.2, 53.8, 73.5, 76.0, 86.7, 113.3, 134.7. MS (EI): *m/z* (%) 278 ([M]$^+$, <1), 237 (18), 181 (10), 137 (10), 127 (11), 95 (15), 81 (48), 75 (100), 69 (19), 59 (28), 55 (23), 43 (21), 41 (30), 28 (34). Found: C, 73.52; H, 10.81. Calcd for $C_{17}H_{30}SiO$: C, 73.31; H, 10.86.

4.2.2. Allyl-(1-ethynyl-5(*S*)-isopropenyl-2-methylcyclohex-2-enyloxy)dimethylsilane (14). Acetylene (430 mL, 19.1 mmol) and 15 mL of dry tetrahydrofuran were cooled down to −78°C then *n*-butyllithium (3.6 mL, 5.7 mmol) and after 30 min at −78°C, (−)-carvone **8** (726 mg, 4.8 mmol) were slowly added. After 1 h stirring at −78°C the reaction mixture was treated with 1N HCl to give, after column chromatography on silica gel (eluent: heptane/diethyl ether, 10:1), the propargylic alcohol (790 mg, 94%). Subsequently, this alcohol (790 mg, 4.5 mmol) was treated with allylchlorodimethylsilane (0.75 mL, 5.0 mmol), DMAP (55 mg, 0.45 mmol) and triethylamine (0.90 g, 8.9 mmol) at room temperature in dry dichloromethane (15 mL) for 16 h. The column was eluted with a heptane/diethyl ether (30:1) mixture to give the silylated enyne **14** (1.07 g, 87%) as a colourless oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.19–0.25 (m, 6H, $Si(CH_3)_2$), 1.68–1.71 (m, 6H, $CH{=}C(CH_3)$, $H_2C{=}C(CH_3)$), 1.75–1.78 (m, 2H, $SiCH_2CH{=}CH_2$), 1.83–2.00 (m, 2H, CH(isopropenyl) CH_2C(quat.)), 2.05–2.27 (m, 2H, $C{=}CHCH_2CH$), 2.54 (s, 1H, $C{\equiv}CH$), 2.45–2.61 (m, 1H, CH_2CH(isopropenyl)CH_2), 4.71–4.74 (m, 2H, $C(CH_3){=}CH_2$), 4.82–4.93 (m, 2H, $SiCH_2CH{=}CH_2$), 5.40–5.46 (m, 1H, $CH_2CH{=}C(CH_3)$), 5.75–6.01 (m, 1H, $SiCH_2CH{=}CH_2$). ^{13}C NMR (50 MHz, $CDCl_3$): δ −0.4, −0.3, 17.5, 20.4, 26.0, 30.8, 39.3, 44.5, 71.1, 73.5, 86.9, 109.1, 113.4, 123.4, 134.2, 137.0, 148.1. MS (EI): *m/z* (%) 274 ([M]$^+$, <1), 233 (21), 173 (17), 77 (12), 76 (10), 75 (100), 59 (17), 41 (10). Found: C, 74.48; H, 9.43. Calcd for $C_{17}H_{26}SiO$: C, 74.39; H, 9.55.

4.2.3. Allyl-(1-ethynyl-2-isopropylidene-5(*R*)-methylcyclohexyloxy)-dimethylsilane (15). Acetylene (345 mL, 15.4 mmol) and 15 mL of dry tetrahydrofuran were cooled down to −78°C then *n*-butyllithium (2.3 mL, 3.7 mmol) and after 30 min at −78°C, (+)-pulegone **9** (469 mg, 3.1 mmol) were slowly added. After 1 h stirring at −78°C the reaction mixture was treated with 1N HCl to give, after column chromatography on silica gel (eluent: heptane/diethyl ether, 15:1), the propargylic alcohol (500 mg, 91%). Subsequently, this alcohol (500 mg, 2.8 mmol) was treated with allylchlorodimethylsilane (0.47 mL, 3.1 mmol), DMAP (34 mg, 0.31 mmol) and triethylamine (568 mg, 5.6 mmol) at room temperature in dry dichloromethane (15 mL) for 16 h. The column was eluted with a heptane/diethyl ether (30:1) mixture to give the silylated enyne **15** (570 mg, 74%) as a colourless oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.22–0.26 (m, 6H, Si(CH_3)$_2$), 0.91 (d, 3H, J=6.5 Hz, CH(CH_3)), 1.43 (t, 2H, J=11.2 Hz, CH(CH$_3$)-CH_2C(quat.)), 1.70 (s, 3H, C═C(CH_3)$_2$), 1.58–1.79 (m, 3H, SiCH_2CH═CH$_2$, CH(CH$_3$)), 2.00 (s, 3H, C═C(CH_3)$_2$), 1.90–2.20 (m, 4H, CH(CH$_3$)CH_2CH_2), 2.59 (s, 1H, C≡CH), 4.80–4.94 (m, 2H, SiCH$_2$CH═CH_2), 5.68–5.94 (m, 1H, SiCH$_2$CH═CH$_2$). ^{13}C NMR (50 MHz, $CDCl_3$): δ 0.0, 21.7, 22.0, 23.7, 26.3, 27.6, 29.4, 33.8, 51.7, 73.5, 77.3, 87.6, 113.4, 126.0, 132.0, 134.5. MS (EI): m/z (%) 276 ([M]$^+$, 1.2), 235 (28), 105 (18), 91 (23), 83 (13), 79 (10), 77 (18), 75 (100), 59 (22), 41 (15), 28 (30). Found: C, 74.05; H, 10.11. Calcd for $C_{17}H_{28}SiO$: C, 73.85; H, 10.21.

4.2.4. Allyl-(1-ethynyl-3,7-dimethyl-octa-2,6-dienyloxy)-dimethylsilane (16). Acetylene (450 mL, 20.1 mmol) and 15 mL of dry tetrahydrofuran were cooled down to −78°C then n-butyllithium (5.0 mL, 8.1 mmol) and after 30 min at −78°C, citral **10** (1.02 g, 6.7 mmol) were slowly added. After 1 h stirring at −78°C the reaction mixture was treated with 1N HCl to give, after column chromatography on silica gel (eluent: heptane/diethyl ether, 15:1), the propargylic alcohol (1.09 g, 91%). Subsequently, this alcohol (1.09 g, 6.1 mmol) was treated with allylchlorodimethylsilane (1.0 mL, 6.7 mmol), DMAP (75 mg, 0.61 mmol) and triethylamine (1.24 g, 12.2 mmol) at room temperature in dry dichloromethane (25 mL) for 16 h. The column was eluted with a heptane/diethyl ether (30:1) mixture to give the silylated enyne **16** (1.59 g, 94%) as a colourless oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.15–0.18 (m, 6H, Si(CH_3)$_2$), 1.50–1.73 (m, 11H, 3×CH_3, SiCH_2CH═CH$_2$), 1.96–2.15 (m, 4H, 2×CH_2), 2.43 (d, 1H, J=2.2 Hz, C≡CH), 4.79–4.94 (m, 2H, SiCH$_2$CH═CH_2), 5.02–5.11 (m, 2H, CH═C(CH$_3$)$_2$, CH(O)(C≡CH)CH═C(CH$_3$)CH$_2$), 5.30–5.37 (m, 1H, CH(O)(C≡CH)CH═C(CH$_3$)CH$_2$), 5.64–5.99 (m, 1H, SiCH$_2$CH═CH$_2$). ^{13}C NMR (50 MHz, $CDCl_3$): δ −1.9, −1.6, 16.4/17.5, 23.0, 24.7, 25.5, 26.0, 32.1, 39.0, 59.1/59.5, 72.0/72.1, 84.4/84.7, 113.2/113.6, 123.5/123.6, 125.0/125.1, 131.5/131.9, 133.6, 137.9/138.2. MS (EI): m/z (%) 276 ([M]$^+$, <1), 145 (15), 117 (13), 105(15), 91 (46), 83(11), 77 (22), 76 (24), 75 (85), 69(95), 61 (16), 59 (29), 45 (19), 43 (16), 41 (100), 39 (24), 28 (21). Found: C, 73.97; H, 10.18. Calcd for $C_{17}H_{28}SiO$: C, 73.85; H, 10.21.

4.2.5. Allyl-[1-(6,6-dimethyl-bicyclo[3.1.1]hep-2-en-2-yl)-prop-2-ynyloxy]-dimethylsilane (17). Acetylene (450 mL, 20.1 mmol) and 15 mL of dry tetrahydrofuran were cooled down to −78°C then n-butyllithium (4.8 mL, 7.6 mmol) and after 30 min at −78°C, (−)-myrtenal **11** (0.95 g, 6.4 mmol) were slowly added. After 1 h stirring at −78°C the reaction mixture was treated with 1N HCl to give, after column chromatography on silica gel (eluent: heptane/diethyl ether, 15:1), the propargylic alcohol (1.09 g, 97%). Subsequently, this alcohol (1.09 g, 6.2 mmol) was treated with allylchlorodimethylsilane (1.03 mL, 6.8 mmol), DMAP (76 mg, 0.62 mmol) and triethylamine (1.25 g, 12.3 mmol) at room temperature in dry dichloromethane (20 mL) for 16 h. The column was eluted with a heptane/diethyl ether (30:1) mixture to give the silylated enyne **17** (1.37 g, 81%) as a colourless oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.10–0.15 (m, 6H, Si(CH_3)$_2$), 0.78–0.82 (m, 3H, CH_3), 1.11–1.18 (m, 1H, C(CH$_3$)$_2$CH(CH$_2$)CH$_2$), 1.21–1.28 (m, 3H, CH_3), 1.52–1.70 (m, 2H, SiCH_2CH═CH$_2$), 2.01–2.12 (m, 1H, C(CH$_3$)$_2$CH(CH$_2$)C═CH), 2.22–2.45 (m, 5H, C≡CH, CH_2, CH_2), 4.69–4.73 (m, 1H, CH(O-silyl)(C≡CH)), 4.81–4.93 (m, 2H, SiCH$_2$CH═CH_2), 5.51–5.59 (m, 1H, C═CHCH$_2$), 5.68–5.90 (m, 1H, SiCH$_2$CH═CH$_2$). ^{13}C NMR (50 MHz, $CDCl_3$): δ −2.1, −2.0, 21.0/21.1, 24.7/24.8, 26.0/26.1, 31.0/31.1, 31.6/31.7, 37.9/38.0, 40.7/40.8, 42.5/42.6, 68.4/68.5, 72.7/72.8, 83.2, 113.3/113.8, 118.4/118.7, 133.9/134.4, 146.3/146.4. MS (EI): m/z (%) 274 ([M]$^+$, <1), 189 (10), 115 (12), 83 (10), 77 (14), 75 (100), 59 (13), 43 (12), 41 (13), 32 (15), 28 (69). Found: C, 74.51; H, 9.48. Calcd for $C_{17}H_{26}SiO$: C, 74.39; H, 9.55.

4.3. General procedure for the preparation of cyclic siloxanes

[RuCl$_2$(p-cymene)]$_2$ (0.5–1.25 mmol%), 1,3-bis(mesityl) imidazolinium chloride and cesium carbonate (molar ratio: 1:2:4) were dissolved in toluene (5 mL per mmol of enyne) and the mixture was stirred for 5 min at room temperature. The enyne (**13**–**17**) was added to the orange–red solution and the mixture was stired at 80°C until GC–MS analysis indicated the complete conversion into the cyclic product. The solvent was then removed and the crude mixture was dissolved in heptane, filtered and evaporated to dryness. For reaction times and purification procedures, see below.

4.3.1. 7(S)-Isopropyl-2,2,10(R)-trimethyl-5-vinyl-1-oxa-2-silaspiro[5.5]undec-4-ene (18). By using 46.2 mg (7.5×10^{-2} mmol, 2.5 mol%) of [RuCl$_2$(p-cymene)]$_2$, 51.8 mg (0.15 mmol, 5 mol%) of 1,3-bis(mesityl)imidazolinium chloride and 98.4 mg (0.30 mmol, 10 mol%) of cesium carbonate in 15 mL of toluene, the total conversion of the enyne **13** (840 mg, 3.02 mmol) was observed after 16 h at 80°C. After a distillation under vacuum, the cyclic compound **18** (640 mg, 76%) was obtained as a colourless oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.10–0.16 (m, 6H, Si(CH_3)$_2$), 0.78–0.94 (m, 9H, 3×CH_3), 1.12–1.42 (m, 4H, CH(CH$_3$)CH_2CH_2), 1.50–1.79 (m, 5H, SiCH_2CH═C(vinyl), CH(CH$_3$)CH_2C (quat.)), 1.87–2.00 (m, 1H, CHCH(CH$_3$)$_2$), 2.27–2.30 (m, 1H, CHCH(CH$_3$)$_2$), 4.80 (dd, 1H, J=10.5, 2.3 Hz, *cis* CH═CH_2), 5.10 (dd, 1H, J=16.6, 2.3 Hz, *trans* CH═CH_2), 5.94 (tm, 1H, J=5.9 Hz, SiCH$_2$CH═C(vinyl)), 6.49–6.66 (m, 1H, CH═CH$_2$). ^{13}C NMR (50 MHz, $CDCl_3$): δ −1.1, 13.6, 19.0, 22.9, 24.5, 27.2, 30.2, 35.1, 51.9, 56.0, 80.7, 113.2, 124.0, 142.0, 146.4. MS (EI): m/z (%) 278 ([M]$^+$, 3), 193 (26), 166 (13), 75 (100), 32 (20), 28 (27). HRMS (EI): 278.2060; $C_{17}H_{30}SiO$ requires 278.2066. Found: C, 73.25; H, 10.95. Calcd for $C_{17}H_{30}SiO$: C, 73.31; H, 10.86.

4.3.2. 10(S)-Isopropenyl-2,2,7-trimethyl-5-vinyl-1-oxa-2-silaspiro[5.5]undeca-4,7-diene (19). By using 14.0 mg (2.3×10^{-2} mmol, 1.25 mol%) of [RuCl$_2$(p-cymene)]$_2$, 15.6 mg (4.6×10^{-2} mmol, 2.5 mol%) of 1,3-bis(mesityl) imidazolinium chloride and 29.7 mg (0.09 mmol, 5 mol%) of cesium carbonate in 8 mL of toluene, the total conversion of the enyne **14** (500 mg, 1.82 mmol) was observed after 16 h at 80°C. After a distillation under vacuum, the cyclic compound **19** (340 mg, 68%) was obtained as a colourless oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.17–0.22 (m, 6H, Si(C*H*$_3$)$_2$), 1.19–1.32 (m, 6H, CH═C(C*H*$_3$), H_2C═C(C*H*$_3$)), 1.51–1.59 (m, 2H, SiC*H*$_2$CH═C(vinyl)), 1.68–1.71 (m, 2H, CH(isopropenyl)C*H*$_2$C(quat.)), 1.92–2.43 (m, 3H, C═CHC*H*$_2$CH, CH$_2$C*H*(isopropenyl)CH$_2$), 4.58–4.92 (m, 4H, C(CH$_3$)═C*H*$_2$, CH═C*H*$_2$) 5.25–5.40 (m, 1H, SiCH$_2$C*H*═C(vinyl)), 5.51–5.64 (m, 1H, CH$_2$C*H*═C(CH$_3$)), 6.08–6.28 (m, 1H, C*H*═CH$_2$). ^{13}C NMR (50 MHz, $CDCl_3$): δ −0.1, 13.6, 18.0, 20.4, 30.8, 38.9, 44.9, 68.7, 108.7, 112.2, 122.5, 125.1, 137.4, 139.2, 149.2, 149.5. MS (EI): *m*/*z* (%) 274 ([M]$^+$, 11), 231 (14), 189 (25), 159 (14), 143 (11), 115 (39), 91 (22), 77 (25), 75 (100), 59 (26), 41 (25). HRMS (EI): 274.1749; $C_{17}H_{26}SiO$ requires 274.1753. Found: C, 74.26; H, 9.60. Calcd for $C_{17}H_{26}SiO$: C, 74.39; H, 9.55.

4.3.3. 7-Isopropylidene-2,2,10(*R*)-trimethyl-5-vinyl-1-oxa-2-silaspiro[5.5]undec-4-ene (20). By using 31.6 mg (5.2×10^{-2} mmol, 2.5 mol%) of [RuCl$_2$(*p*-cymene)]$_2$, 35.4 mg (0.103 mmol, 5 mol%) of 1,3-bis(mesityl)imidazolinium chloride and 67.3 mg (0.207 mmol, 10 mol%) of cesium carbonate in 10 mL of toluene, the total conversion of the enyne **15** (570 mg, 2.07 mmol) was observed after 16 h at 80°C. After a distillation under vacuum, the cyclic compound **20** (350 mg, 62%) was obtained as a colourless oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.20–0.25 (m, 6H, Si(C*H*$_3$)$_2$), 0.90 (d, 3H, *J*=6.1 Hz, CH(C*H*$_3$)), 1.43–1.50 (m, 2H, CH(CH$_3$)C*H*$_2$C(quat.)), 1.72 (s, 3H, C═C(C*H*$_3$)$_2$), 1.58–1.84 (m, 3H, SiC*H*$_2$CH═CH$_2$, C*H*(CH$_3$)), 1.98 (s, 3H, C═C(C*H*$_3$)$_2$), 1.95–2.22 (m, 4H, CH(CH$_3$)C*H*$_2$C*H*$_2$), 4.72 (dd, 1H, *J*=10.5, 2.1 Hz, *cis* CH═C*H*$_2$), 5.19 (dd, 1H, *J*=17.0, 2.1 Hz, *trans* CH═C*H*$_2$), 6.02–6.09 (m, 1H, SiCH$_2$C*H*═C(vinyl)), 6.14–6.31 (m, 1H, C*H*═CH$_2$)). ^{13}C NMR (50 MHz, $CDCl_3$): δ 0.6, 13.3, 22.0/22.4, 23.4, 25.8, 26.6, 30.4, 47.7, 79.3, 111.9, 121.0, 130.2, 133.2, 139.5, 148.1. MS (EI): *m*/*z* (%) 276 ([M]$^+$, 7), 261 (12), 219 (12), 187 (22), 179 (14), 131 (18), 91 (27), 77 (19), 75 (100), 59 (12), 41 (14). HRMS (EI): 276.1906; $C_{17}H_{28}SiO$ requires 276.1909. Found: C, 73.75; H, 10.23. Calcd for $C_{17}H_{28}SiO$: C, 73.85; H, 10.21.

4.3.4. 6-(2,6-Dimethyl-hepta-1,5-dienyl)-2,2-dimethyl-5-vinyl-3,6-dihydro-2*H*-[1,2]oxasi-line (21). By using 23.2 mg (3.8×10^{-2} mmol, 2.5 mol%) of [RuCl$_2$(*p*-cymene)]$_2$, 26.0 mg (7.6×10^{-2} mmol, 5 mol%) of 1,3-bis(mesityl)imidazolinium chloride and 49.5 mg (0.15 mmol, 10 mol%) of cesium carbonate in 7.5 mL of toluene, 26% of conversion of the enyne 16 (420 mg, 1.5 mmol) was observed after 48 h at 80°C. The cyclic compound **21** was not separated from the starting enyne but observed in GC–MS. MS (EI): *m*/*z* (%) 276 ([M]$^+$, 5), 171 (21), 125 (12), 123 (34), 91 (16), 77 (28), 75 (75), 69(28), 43 (31), 41 (100), 39 (12)). Found: C, 73.79; H, 10.29. Calcd for $C_{17}H_{28}SiO$: C, 73.85; H, 10.21.

4.3.5. 6-(6,6-Dimethyl-bicyclo[3.1.1]hept-2-en-2-yl)-2,2-dimethyl-5-vinyl-3,6-dihydro-2*H*-[1,2]oxasiline (22). By using 55.8 mg (9.1×10^{-2} mmol, 2.5 mol%) of [RuCl$_2$(*p*-cymene)]$_2$, 62.5 mg (0.182 mmol, 5 mol%) of 1,3-bis(mesityl)imidazolinium chloride and 118.9 mg (0.365 mmol, 10 mol%) of cesium carbonate in 18 mL of toluene, the total conversion of the enyne **17** (1.0 g, 3.65 mmol) was observed after 16 h at 80°C. After a distillation under vacuum, the cyclic compound **22** (651 mg, 65%) was obtained as a colourless oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.04–0.15 (m, 6H, Si(C*H*$_3$)$_2$), 0.72–0.77 (m, 3H, C*H*$_3$), 1.08–1.14 (m, 1H, C(CH$_3$)$_2$C*H*(CH$_2$)CH$_2$), 1.18–1.24 (m, 3H, C*H*$_3$), 1.38–1.43 (m, 2H, SiC*H*$_2$CH═CH$_2$), 1.99–2.05 (m, 1H, C(CH$_3$)$_2$C*H*(CH$_2$)C═CH), 2.11–2.25 (m, 2H, C*H*$_2$), 2.30–2.40 (m, 2H, C*H*$_2$), 4.80–5.03 (m, 3H, *trans* CH═C*H*$_2$, C*H*(O-silyl), SiCH$_2$C*H*═C(vinyl)), 5.35 (m, 1H, *cis* CH═C*H*$_2$), 6.02–6.08 (m, 1H, C═C*H*CH$_2$), 6.13–6.27 (m, 1H, C*H*═CH$_2$). ^{13}C NMR (50 MHz, $CDCl_3$): δ 0.5, 0.8, 13.6/13.7, 21.2/21.5, 26.3, 31.2/31.3, 31.7/31.8, 37.9, 40.6/40.7, 43.0/43.1, 75.1/75.6, 110.7/110.9, 118.9/119.1, 127.9/128.1, 138.1/138.2, 147.4, 148.1. MS (EI): *m*/*z* (%) 274 ([M]$^+$, <1), 91 (13), 77 (12), 75 (100), 69 (59), 41 (30), 32 (17), 28 (85). HRMS (EI): 274.1750; $C_{17}H_{26}SiO$ requires 274.1753. Found: C, 74.24; H, 9.52. Calcd for $C_{17}H_{26}SiO$: C, 74.39; H, 9.55.

4.4. Preparation of the diols 23 and 24

4.4.1. 1-(3-Hydroxy-1-vinylpropenyl)-2(*S*)-isopropyl-5(*R*)-methylcyclohexanol (23). H_2O_2 (6.6 mL, 64.7 mmol) was added to a solution of the cyclic siloxane **18** (0.45 g, 1.6 mmol), KF (0.47 g, 8.1 mmol) and $KHCO_3$ (0.38 g, 3.7 mmol) in 15 mL of THF and 15 mL of methanol. After 24 h at 40°C, the reaction mixture was extracted with diethyl ether (3×10 mL) and the diol **23** (264 mg, 68%) was isolated as a colourless oil after flash chromatography on silica gel with diethyl ether as eluent. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.74 (d, 3H, *J*=6.9 Hz, C*H*$_3$), 0.82 (d, 3H, *J*=6.9 Hz, CH(C*H*$_3$)$_2$), 0.91 (d, 3H, *J*=7.0 Hz, CH(C*H*$_3$)$_2$), 1.20–1.50 (m, 6H, CHC*H*$_2$C*H*$_2$CHC*H*$_2$), 1.60–2.00 (m, 3H, C(OH)CH$_2$C*H*CH$_3$, C*H*CH(CH$_3$)$_2$, CHC*H*(CH$_3$)$_2$), 4.58–4.65 (m, 2H, C═CHC*H*$_2$OH), 5.05 (dd, 1H, *J*=10.7, 2.0 Hz, *cis* CH═C*H*$_2$), 5.42 (dd, 1H, *J*=16.1, 2.0 Hz, *trans* CH═C*H*$_2$), 5.90–5.93 (m, 1H, C═C*H*CH$_2$OH), 6.36–6.50 (m, 1H, C*H*═CH$_2$). ^{13}C NMR (50 MHz, $CDCl_3$): δ 18.4, 23.3, 23.9, 26.2, 29.8, 34.9, 49.8, 53.0, 72.8, 76.0, 115.9, 122.8, 132.0, 144.7. MS (EI): *m*/*z* (%) 238 ([M]$^+$, <1), 220 (19), 136 (15), 135 (100), 107 (19), 93 (11), 91 (26), 79 (41), 77 (26), 69 (20), 67 (14), 65 (17), 55 (40), 53 (14), 43 (27), 41 (64), 39 (27). Found: C, 75.28; H, 10.52. Calcd for $C_{15}H_{26}O_2$: C, 75.58; H, 10.99.

4.4.2. 1-(6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-yl)-2-vinylbut-2-ene-1,4-diol (24). H_2O_2 (2.7 mL, 29.1 mmol) was added to a solution of the cyclic siloxane **22** (0.20 g, 0.73 mmol), KF (0.21 g, 3.6 mmol) and $KHCO_3$ (0.17 g, 2.3 mmol) in 7 mL of THF and 7 mL of methanol. After 24 h at 40°C, the reaction mixture was treated as described above to give the diol **24** (139 mg, 82%) as a colourless oil, after flash chromatography on silica gel with diethyl ether as eluent. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.79 (s, 3H, C*H*$_3$), 1.07–1.15 (m, 1H, C(CH$_3$)$_2$C*H*(CH$_2$)CH$_2$), 1.23 (s, 3H, C*H*$_3$), 2.04–2.17 (m, 1H, C(CH$_3$)$_2$C*H*(CH$_2$)C═CH), 2.23–2.47 (m, 4H, C*H*$_2$, C*H*$_2$), 2.80 (broad s, 2H, 2×OH), 4.19–4.38 (m, 2H, C═CHC*H*$_2$OH), 4.90–5.07 (m, 2H, C*H*(OH), *cis* CH═C*H*$_2$), 5.25–5.37 (m, 1H, *trans* CH═C*H*$_2$), 5.49–5.57 (m, 1H, CH(OH)C═C*H*CH$_2$), 5.90 (t, 1H, *J*=6.8 Hz, C*H*═CH$_2$OH), 6.19–6.32 (m, 1H, C*H*═CH$_2$). ^{13}C NMR (50 MHz, $CDCl_3$): δ 21.1/21.2, 26.1, 31.2, 31.7, 37.8/37.9, 40.7/40.8, 43.0/43.1, 58.6/58.9, 71.3/71.6, 114.2/114.5, 117.7/118.2, 130.6/130.7, 137.2/137.3, 140.1/140.3, 147.4/147.8. MS (EI): *m/z* (%) 234 ([M]$^+$, 4), 219 (14), 193 (16), 169 (21), 155 (20), 129 (18), 103 (21), 91 (14), 77 (32), 75 (100), 59 (20), 43 (12), 41 (30). Found: C, 76.38; H, 9.40. Calcd for $C_{15}H_{22}O_2$: C, 76.88; H, 9.46.

4.5. Preparation of the polyenes 25 and 26

4.5.1. 1(*S*)-Isopropyl-4(*R*)-methyl-2-(1-vinylprop-2-enylidene)cyclohexane (25). *n*-Bu_4NF (1.65 mL, 1.65 mmol) was added at −78°C to a solution of the cyclic siloxane **18** (153 mg, 0.55 mmol) in 5 mL of THF and 5 mL of CH_2Cl_2. After 16 h at room temperature and purification by flash chromatography with heptane as eluent, the polyene **25** (79 mg, 70%) was obtained as a colourless oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.76 (d, 3H, *J*=6.7 Hz, C*H*$_3$), 0.92 and 0.94 (2×d, 6H, *J*=7.2 Hz, CH(C*H*$_3$)$_2$), 1.15–1.32 (m, 4H, CHC*H*$_2$C*H*$_2$CHCH$_2$), 1.53–1.87 (m, 2H, C*H*(CH$_3$), CHC*H*(CH$_3$)$_2$), 1.96–2.21 (m, 2H, CHC(=C)C*H*$_2$), 2.44–2.58 (m, 1H, C*H*C(=C)CH$_2$), 5.08–5.25 (m, 4H, 2×(CH=C*H*$_2$)), 6.42–6.69 (m, 2H, 2×(C*H*=CH$_2$)). ^{13}C NMR (50 MHz, $CDCl_3$): δ 18.1, 20.8, 23.7, 27.1, 29.7, 30.5, 32.4, 45.1, 116.1, 116.8, 132.9, 134.3, 134.5, 140.8. MS (EI): *m/z* (%) 204 ([M]$^+$, 19), 161 (40), 133 (20), 119 (32), 117 (12), 107 (18), 105 (83), 93 (48), 91 (100), 83 (18), 81 (65), 79 (51), 77 (40), 69 (28), 67 (36), 55 (37), 41 (43), 39 (18). Found: C, 88.26; H, 11.72. Calcd for $C_{15}H_{24}$: C, 88.16; H, 11.84.

4.5.2. 6,6-Dimethyl-2-(2-vinylbuta-1,3-dienyl)-bicyclo[3.1.1]hept-2-ene (26). *n*-Bu_4NF (1.65 mL, 1.65 mmol) was added at −78°C to a solution of the cyclic siloxane **22** (150 mg, 0.55 mmol) in 5 mL of THF and 5 mL of CH_2Cl_2. After 16 h at room temperature and purification by flash chromatography with heptane as eluent, the polyene **26** (69 mg, 63%) was obtained as a colourless oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.88 (s, 3H, C*H*$_3$), 1.14–1.27 (m, 1H, C(CH$_3$)$_2$C*H*(CH$_2$)CH$_2$), 1.30 (s, 3H, C*H*$_3$), 2.03–2.13 (m, 1H, C(CH$_3$)$_2$C*H*(CH$_2$)C=CH), 2.37–2.45 (m, 4H, C*H*$_2$, C*H*$_2$), 5.06–5.42 (m, 4H, (2×CH=C*H*$_2$)), 5.63–5.69 (m, 1H, CHC=C*H*CH$_2$), 5.96–6.01 (m, 1H, C*H*=C(vinyl)$_2$), 6.35–6.49 (m, 1H, C*H*=CH$_2$), 6.58–6.72 (m, 1H, C*H*=CH$_2$). ^{13}C NMR (50 MHz, $CDCl_3$): δ 21.1, 26.2, 31.5, 32.2, 37.7, 40.2, 46.3, 114.6, 116.7, 126.3, 131.0, 135.4, 138.1, 144.3, 146.8. MS (EI): *m/z* (%) 200 ([M]$^+$, 25), 157 (19), 130 (68), 128 (24), 116 (30), 103 (11), 91 (100), 79 (12), 77 (30), 65 (15), 53 (21), 51 (14), 41 (44), 39 (30). Found: C, 88.19; H, 11.78. Calcd for $C_{15}H_{24}$: C, 88.16; H, 11.84.

4.6. Preparation of the terpenes 27 and 28

4.6.1. 2-(1-Ethylpropylidene)-1(*S*)-isopropyl-4(*R*)-methylcyclohexane (27). Cyclic siloxane **18** (300 mg, 1.08 mmol) was added to Pd/C (30 mg, 10 wt%) in 10 mL of dichloromethane. After removal of the nitrogen atmosphere by hydrogen, the reaction mixture was stirred 16 h at room temperature under 1 atm of hydrogen. After filtration on celite and purification of the crude product by chromatography over silica gel with heptane, the terpene **27** (117 mg, 52%) was isolated as a colourless oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.82–0.90 (m, 15H, 5×C*H*$_3$), 1.16–1.29 (m, 4H, C*H*$_2$C*H*$_2$), 1.40–1.48 (m, 2H, C*H*(CH$_3$)$_2$, C*H*(CH$_3$)), 1.59–1.80 (m, 6H, C*H*$_2$C=C(C*H*$_2$CH$_3$)$_2$), 1.88–1.98 (m, 1H, C*H*CH(CH$_3$)$_2$. ^{13}C NMR (50 MHz, $CDCl_3$): δ 13.5/13.8, 20.8, 23.8/23.9, 27.0, 27.3, 27.4, 29.8, 35.3, 42.0, 47.1, 140.9, 146.1. MS (EI): *m/z* (%) 208 ([M]$^+$, 12), 165 (61), 123 (33), 109 (74), 95 (100), 93 (18), 81 (56), 79 (28), 69 (26), 67 (47), 55 (52), 53 (17), 43 (33), 41 (64), 39 (11). Found: C, 86.36; H, 13.49. Calcd for $C_{15}H_{28}$: C, 86.46; H, 13.54.

4.6.2. 2-(2-Ethylbutyl)-6,6-dimethylbicyclo[3.1.1]heptane (28). Cyclic siloxane **22** (150 mg, 0.55 mmol) was added to Pd/C (15 mg, 10 wt%) in 5 mL of dichloromethane. After removal of the nitrogen atmosphere by hydrogen, the reaction mixture was stirred 16 h at room temperature under 1 atm of hydrogen. After filtration on celite and purification of the crude product by chromatography over silica gel with heptane, the terpene **28** (49 mg, 43%) was isolated as a colourless oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.80–1.09 (m, 22H, 4×C*H*$_3$, 5×C*H*$_2$), 1.05–1.14 (m, 1H, C(CH$_3$)$_2$C*H*(CH$_2$)CH$_2$), 1.26–1.44 (m, 5H, CHC*H*$_2$C*H*C*H*CH$_2$C*H*Et$_2$). ^{13}C NMR (50 MHz, $CDCl_3$): δ 10.2/10.5, 19.5, 21.0/21.4, 26.2, 28.5, 28.8, 31.0/31.1, 31.6, 37.8, 39.9, 44.0, 46.8. MS (EI): *m/z* (%) 208 ([M+1]$^+$, 7), 165 (26), 119 (26), 91 (100), 89 (29), 75 (73), 73 (16), 61 (22), 59 (49), 43 (15), 41 (22).). Found: C, 86.41; H, 13.52. Calcd for $C_{15}H_{28}$: C, 86.46; H, 13.54.

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