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Metalated epoxides as carbenoids. Competing C–H and C=C insertion in α-alkoxy epoxide systems

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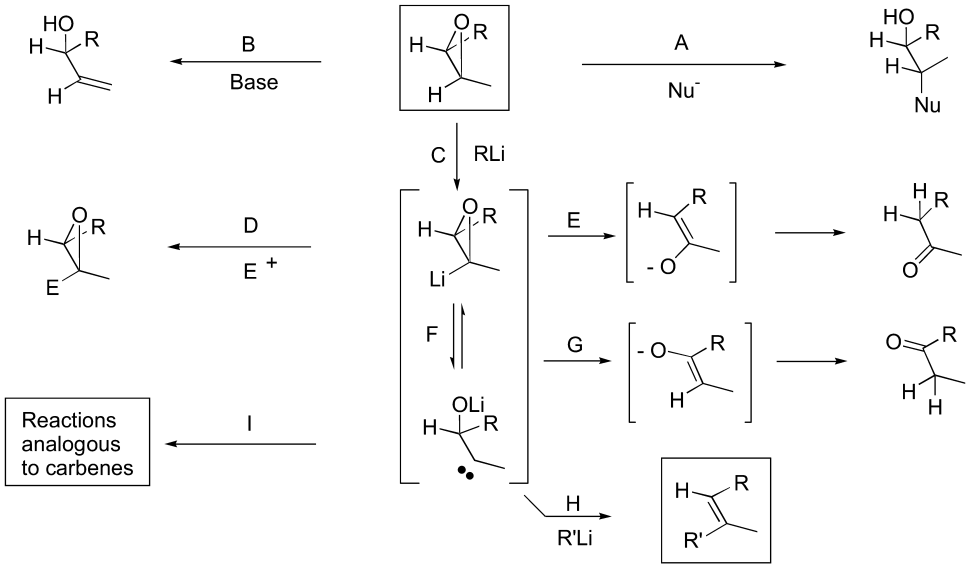
Abstract—In a reinvestigation of the reactivity of carbenoids derived from epoxides, we studied the factors that could influence the chemoselectivity of the carbenoid insertion into vicinal C–H or C=C bond in cyclic α-alkoxy epoxides bearing an alkenyl side chain. This reaction gives access to bi- or tricyclic systems, respectively.

1. Introduction

Epoxides are versatile intermediates of wide scope and applicability in synthetic organic chemistry. Their chemical reactivity is due, in part, to the basicity of the oxygen atom but also to the ring strain of the three-membered heterocycle. Under the influence of a strong organolithium base, the oxirane ring may engage in various types of reactions.[1]

The nucleophilic attack of base on the oxirane ring (since the lithium base can also act as a nucleophile) is a known route to substituted alcohols[2] (Scheme 1, path A). This reaction usually proceeds through a S_N2 type process at the less hindered carbon atom. The second well known reaction involving an epoxide and a strong base is β-elimination[3] which provides easy access to allylic alcohols[4] (Scheme 1, path B). This reaction, which takes place via *syn*



Scheme 1.

Keywords: carbenoids; cycloaddition; cyclopropanes; epoxides; insertion.
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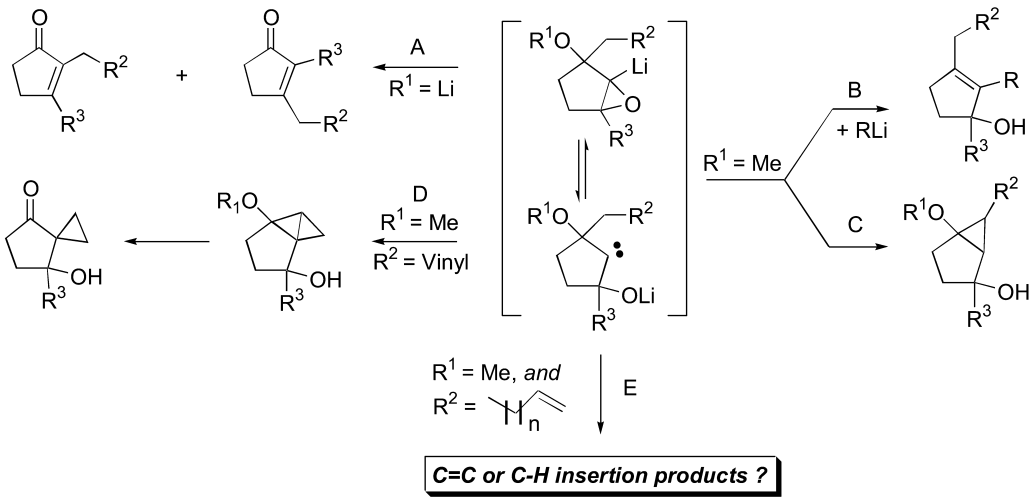


Scheme 2.

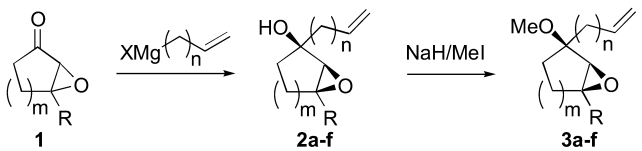
elimination,[5] may afford optically active alcohols when a chiral base is used on *meso* substrates.[6] The third possibility that is depicted in Scheme 1 is the direct metallation of the oxirane ring which produces a carbenoid species[7] (path C). We and others have surveyed the diverse behavior of these epoxide-derived carbenoids.[8] The metalated epoxide can be trapped by various electrophiles[9] (path D), but it may also undergo β-elimination[10] to provide, after hydrolysis, a ketone (path E). We found that the carbene character of the key intermediate (resulting from the carbon–oxygen bond cleavage) depended on the solvent[11] (path F). This intermediate may engage in reactions similar to a carbene. These include dimerizations,[12] C–H insertions,[13] [2+1] cycloadditions[14] (path I). However, it may also rearrange via a hydride-1,2-shift[15] (path G). This leads to the formation of a ketone. The last example illustrated in Scheme 1 is the reductive alkylation of the starting epoxide[16] (path H). This reaction takes place by insertion of the carbene-like species into the carbon–lithium bond of the base, followed by instantaneous lithium oxide elimination to afford substituted alkenes.

The reactivity of these epoxide-derived carbenoids in substituted cyclic systems is different. Indeed, we demonstrated that in cyclic α-hydroxy epoxides, an alkyl 1,2-shift lead to α,β-unsaturated ketones (Scheme 2, path A).[17] Also, we showed that the insertion of the organolithium reagent, followed by alkoxide elimination, was predominant in α-alkoxy epoxides (pathway B).[18] The latter route produced allylic alcohols in high yield. An enantioselective version of this process has recently been developed by Hodgson et al.[19] However, in some instances, we observed the formation of cyclopropanes which arose from the insertion of the carbenoid into an adjacent C–H bond (path C).[20] Finally, when R^1=alkyl and R^2=vinyl, an intramolecular [2+1] cycloaddition afforded a highly strained tricyclic intermediate (path D).[21] The facile hydrolysis of this intermediate under mildly acidic conditions provided a novel route to spirocyclopropanes.[22]

The objective of this article is to report our investigations on the factors that govern the chemoselectivity of the carbenoid intermediate towards insertion into C–H or C=C bonds (Scheme 2, pathway E). In particular, the influence of the length of the alkene side chain, the size of the carbocycle and the solvent effect were studied.

2. Results and discussion

Initially, substituted cyclic α-methoxy epoxides were synthesized according to Scheme 3. The nuclephilic addition of different alkene-Grignard reagents on cycloalkenone oxides **1** afforded *syn* α-hydroxy epoxides **2** in nearly quantitative yield. The *syn* selectivity of this process has already been observed and commented on by others.[23] Protection of the hydroxyl group of **2** by methyl iodide furnished the starting ether-epoxides **3**. Five and six-membered ring epoxides were prepared by this route.

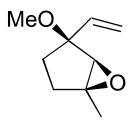
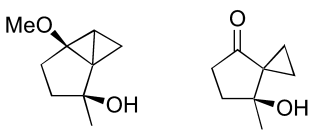
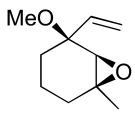
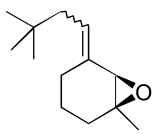
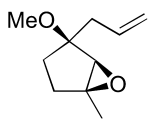
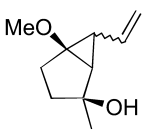
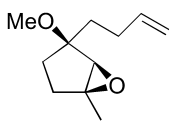
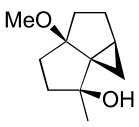
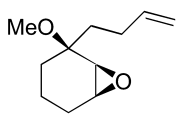
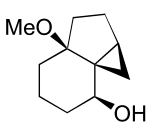
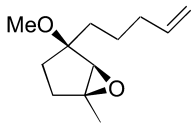
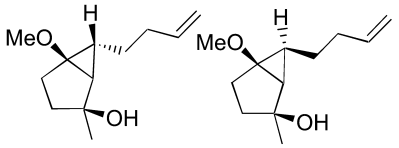


Scheme 3.

As already mentioned in the introduction, carbenoids derived from α-methoxy epoxides can undergo either [2+1] cycloadditions (when adjacent to a C=C bond) or insertion into a neighboring C–H bond. The influence of the alkene side chain on the product distribution was studied by reacting epoxy ethers **3** with *n*-butyllithium in pentane, at room temperature (see Section 4). Pentane was chosen as solvent since we demonstrated in a previous investigation that it was the solvent of choice to minimize insertion of the carbenoid into the C–Li bond of the base (reductive alkylation process).[20] The results are summarized in Table 1.

Obviously, when the vinyl-substituted five-membered ring epoxy ether (Table 1, entry a) was reacted under the above mentioned conditions, the only product that was detected resulted from the insertion of the carbenoid into the C=C bond. This product is however, highly unstable and readily undergoes ring opening by a S_E2 type process to cleanly

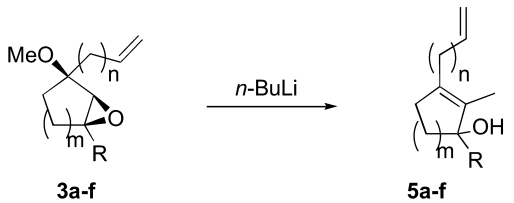
Table 1. : Examples of reactivity of various cyclic epoxy ether **3**

Entry	Substrate **3**	Product **4**	Yield[a]
a			88[b]
b			61
c			<25[c]
d			47
e			37
f			57[d]

[a] Isolated yield.
[b] Yield of rearranged spiro product.
[c] ^{1}H NMR spectroscopy yield.
[d] Combined yield.

give a spiro cyclopropane. Surprisingly, the corresponding six-membered ring substrate (Table 1, entry b) failed to react in a similar fashion. Rather, a product that results from S_N2 prime attack of the lithium base on the vinylogous system was obtained.[24] The same holds true when the more basic *tert*-butyllithium was used giving alkene **4b** as a 50:50 mixture of *Z* and *E* isomers (entry b). This difference in reactivity between five- and six-membered ring systems can be attributed, in part, to the specific conformation of the latter substrate in which the leaving methoxy group is able to adopt an axial position. This is favorable to the *syn* S_N2 prime process. When an allyl side chain was introduced on the starting epoxy ether (entry c), C–H insertion was predominant. By ^{1}H NMR spectroscopy we detected the two diastereomers of the cyclopropane ring together with C–Li insertion products. No product arising from C=C insertion was observed. The intramolecular C–H insertion is probably favored due to allylic activation of the C–H bond. The yield (determined by ^{1}H NMR spectroscopy) of this transformation appears however to be poor (<25%) and our attempts to isolate the compounds of interest by chromatography resulted in decomposition of the labile cyclopropane. The incorporation of a homo-allyl side chain next to the methoxy group (entry d) permitted [2+1] cycloaddition of the carbenoid species with the proximal C=C bond. The same reactivity was observed with the six-membered ring epoxy ether (entry e). The cyclopropanes were obtained in each case as single diastereomers. This result can be ascribed to the geometric constraint of the tricyclic system that precludes formation of other diastereoisomers. Finally, the last example illustrated in Table 1 is the pentenyl substituted substrate which reacted with the C–H bond to give the inserted product in 57% yield as a 60:40 mixture of *trans* and *cis* isomers (entry f).[25] In this example, the carbenoid is too far from the C=C bond to react by cycloaddition. Intramolecular C–H insertion was therefore favored.

It is to be noted that we observed, in most of the examples studied, the formation of a product that arises from insertion of butyllithium in the carbenoid species (Scheme 4). This afforded cyclic allylic alcohols **5a–e** after MeOLi elimination. This reductive alkylation process, which was



3a-f **5a-f**

Scheme 4.

originally described by us,[18] is also competing with C–H and C=C insertions.

3. Conclusion

The chemoselective intramolecular carbenoid insertion into C–H and C=C bonds in cyclic α-alkoxy epoxides allows the synthesis of bi- and tri-cyclic systems, respectively. If the vicinal C–H bond is allylic (as in substrate **3c**) or if there is at least four carbon atoms between the carbenoid and the double bond, C–H insertion takes place selectively. In other cases, [2+1] cycloaddition, leading to tricyclic systems, is the sole intramolecular reaction.

4. Experimental

4.1. General

^{1}H and ^{13}C NMR spectra were respectively recorded on a Bruker ARX 250 spectrometer at 250 and 62.9 MHz; chemical shifts are reported in ppm from TMS. All reaction were performed under argon. Column chromatography were performed on silica gel, 230–400. TLC were run on Merck Kieselgel 60F_{254} plates. THF was distilled from sodium/benzophenone ketyl. Pentane was dried by distillation over Na.

4.2. General procedure for the synthesis of α-hydroxy epoxides 2a–f

Synthesis of 2-hydroxy-5-methyl-2-Prop-2-enyl-6-oxa-bicyclo[3.1.0]hexane (**2c**). Allylmagnesium bromide (2 mL of 2.0 M soln/diethyl ether, 1.12 equiv.) was added dropwise at 0°C to a solution of 3-methyl cyclopentenone oxide (0.200 g, 1.78 mmol, 1 equiv.) in 18 mL of THF. The mixture was stirred for 30 min at 0°C, quenched with saturated NH_4Cl and extracted three times with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was used without further purification in the next step (oil, 0.25 g, 91%).

4.2.1. 2-Hydroxy-5-methyl-5-vinyl-6-oxa-bicyclo[3.1.0]-hexane (2a). (Oil, 85%). ^{1}H NMR ($CDCl_3$): δ=1.39 (s, 3H), 1.40 (m, 3H), 1.94 (m, 1H), 3.05 (s, 1H), 5.07 (d, J=10.8 Hz, 1H), 5.16 (d, J=17.6 Hz 1H), 5.73 (dd, J=10.8, 17.6 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ=17.3, 29.8, 34.2, 63.6, 66.9, 78.5, 113.4, 138.6.

4.2.2. 2-Hydroxy-6-methyl-2-vinyl-7-oxa-bicyclo[4.1.0]-heptane (2b). (Oil, 64%). ^{1}H NMR ($CDCl_3$): δ=1.35 (s, 3H), 1.45 (m, 1H), 1.50–1.78 (m, 3H), 1.87–1.95 (m, 2H), 2.91 (s, 1H), 5.20 (d, J=10.7 Hz, 1H), 5.35 (d, J=17.7 Hz 1H), 5.95 (dd, J=10.7, 17.7 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ=16.7, 24.0, 28.9, 34.4, 62.0, 65.2, 70.7, 114.6, 141.5.

4.2.3. 2-Hydroxy-5-methyl-2-prop-2-enyl-6-oxa-bicyclo[3.1.0]hexane (2c). (Oil, 91%). ^{1}H NMR ($CDCl_3$): δ=1.56 (s, 3H), 1.57–1.78 (m, 3H), 1.90 (m, 1H), 2.20–2.35 (m, 2H), 3.03 (s, 1H), 5.04–5.12 (m, 2H), 5.75–5.90 (m, 1H). ^{13}C NMR ($CDCl_3$): δ=18.1, 30.7, 34.0, 41.4, 64.7, 68.3, 80.3, 118.8, 134.4.

4.2.4. 2-But-3-enyl-5-methyl-2-hydroxy-6-oxa-bicyclo[3.1.0]hexane (2d).[17] (Oil, 81%) ^{1}H NMR ($CDCl_3$): δ=1.40 (s, 3H), 1.47–1.62 (m, 4H), 1.90–2.01 (m, 2H), 2.12–2.20 (m, 2H), 3.08 (s, 1H), 4.92–5.07 (m, 2H), 5.74–5.96 (m, 1H). ^{13}C NMR ($CDCl_3$): δ=18.1, 27.6, 30.8, 34.1, 35.6, 64.3, 68.4, 80.2, 114.7, 138.6.

4.2.5. 2-Hydroxy-5-methyl-2-pent-4-enyl-6-oxa-bicyclo[3.1.0]hexane (2f). (Oil, 95%) ^{1}H NMR ($CDCl_3$): δ=1.41 (s, 3H), 1.44–1.61 (m, 5H), 1.68 (m, 1H), 1.95 (m, 2H), 2.06–2.15 (m, 2H), 3.06 (s, 1H), 4.93–5.03 (m, 2H), 5.81 (m, 1H). ^{13}C NMR ($CDCl_3$): δ=19.0, 22.4, 30.7, 33.7, 34.1, 35.7, 64.2, 68.4, 80.2, 114.8, 138.4.

4.3. General procedure for the synthesis of α-methoxy epoxides 3a–f

Synthesis of 2-methoxy-5-methyl-2-prop-2-enyl-6-oxa-bicyclo[3.1.0]hexane (**3c**). Crude alcohol **2c** (0.25 g, 1.62 mmol, 1 equiv.) was taken up in 16 mL THF and NaH (0.078 g of a 60% suspension in oil, 1.2 equiv.) was added portionwise. After 5 min., methyl iodide (0.16 mL, 1.6 equiv.) was added dropwise. The mixture was stirred at room temperature for 3 h. The reaction was then quenched with H_2O and extracted twice with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was chromatographed on silica (EtOAc/hexane, 5:95) to yield pure **3c** (oil, 0.20 g, 73%).

4.3.1. 2-Methoxy-5-methyl-2-vinyl-6-oxabicyclo[3.1.0]-hexane (3a).[22] (Oil, 85%). ^{1}H NMR ($CDCl_3$): δ=1.31 (s, 3H), 1.41–1.70 (m, 3H), 1.85–1.96 (m, 1H), 3.18 (s, 1H), 3.20 (s, 3H), 5.07 (d, J=17.8 Hz, 1H), 5.16 (d, J=10.3 Hz 1H), 5.73 (dd, J=10.3, 17.8 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ=17.8, 29.6, 30.1, 52.3, 62.6, 63.7, 84.9, 115.7, 138.6.

4.3.2. 2-Methoxy-6-methyl-2-vinyl-7-oxabicyclo[4.1.0]-heptane (3b). (Oil, 79%). ^{1}H NMR ($CDCl_3$): δ=1.15 (m, 1H), 1.36 (s, 3H), 1.46 (m, 1H), 1.59–1.89 (m, 4H), 3.01 (s, 1H), 3.34 (s, 3H), 5.20 (d, J=14.8 Hz, 1H), 5.35 (d, J=9.1 Hz 1H), 5.82 (dd, J=14.8, 9.1 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ=17.8, 24.3, 28.4, 30.2, 51.0, 60.1, 61.7, 76.9, 117.0, 140.2.

4.3.3. 2-Methoxy-5-methyl-2-prop-2-enyl-6-oxa-bicyclo[3.1.0]hexane (3c). (Oil, 73%). ^{1}H NMR ($CDCl_3$): δ=1.34 (s, 3H), 1.62 (m, 2H), 1.90 (m, 2H), 2.25 (m, 2H), 3.05 (s, 1H), 3.28 (s, 3H), 5.02 (m, 2H), 5.77 (m, 1H).

4.3.4. 2-But-3-enyl-2-methoxy-5-methyl-6-oxa-bicyclo[3.1.0]hexane (3d). (Oil, 76%) ^{1}H NMR ($CDCl_3$): δ=1.55 (s, 3H), 1.58–1.78 (m, 5H), 2.07 (m, 1H), 2.27 (m, 2H), 3.25 (s, 1H), 3.46 (s, 3H), 5.06–5.21 (m, 2H), 5.96 (m, 1H). ^{13}C NMR ($CDCl_3$): δ=18.0, 27.1, 28.3, 30.0, 32.9, 51.6, 61.8, 65.1, 84.1, 114.5, 138.5.

4.3.5. 2-But-3-enyl-2-methoxy-7-oxabicyclo[4.1.0]hep-tane (3e). (Oil, 70%) ^{1}H NMR ($CDCl_3$): δ=1.05–1.30 (m, 2H), 1.40–1.55 (m, 3H), 1.60–2.15 (m, 5H), 2.93 (d,

J=4 Hz, 1H), 3.16 (m, 1H), 3.29 (s, 3H), 4.87–5.02 (m, 2H), 5.77 (m, 1H). ^{13}C NMR ($CDCl_3$): δ=16.7, 23.5, 26.8, 29.2, 34.1, 50.2, 53.1, 56.4, 74.4, 114.5, 138.6.

4.3.6. 2-Methoxy-5-methyl-2-pent-4-enyl-6-oxabicyclo[3.1.0]hexane (3f). (Oil, 87%) ^{1}H NMR ($CDCl_3$): δ=1.39 (s, 3H), 1.41–1.63 (m, 7H), 1.92 (m, 1H), 2.06 (m, 2H), 3.09 (s, 1H), 3.32 (s, 3H), 4.94–5.04 (m, 2H), 5.79 (m, 1H). ^{13}C NMR ($CDCl_3$): δ=18.1, 22.1, 28.4, 30.1, 33.3, 34.1, 51.6, 61.8, 65.3, 84.3, 114.8, 138.4.

4.4. A typical experimental procedure is given for products obtained in entry d, Table 1

Under Ar, at room temperature *n*-BuLi (0.69 mL of a 1.6 M solution in hexanes, 2 equiv.) was added dropwise, over a period of 20 min, to a stirred solution of 2-but-3-enyl-2-methoxy-5-methyl-6-oxabicyclo[3.1.0]hexane **3d** (0.1 g, 0.55 mmol, 1 equiv.) in 11 mL of anhydrous pentane. The mixture was stirred at room temperature for 5 min. The reaction was then quenched with H_2O, extracted twice with CH_2Cl_2, dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The crude product was chromatographed over silica (EtOAc/hexane, 2:8) to yield two products (**4d**: C=C insertion product and **5d**: C–Li insertion product).

4.4.1. 7-Hydroxy-7-methyl-spiro[2.4]heptan-4-one (4a). Phenyllithium in Et_2O (0.05 M) was used as base in this case as recently reported.[22] The isolated product in this case is the rearranged spiro cyclopropane product (oil, 88%). ^{1}H NMR ($CDCl_3$): δ=0.91 (m, 4H), 1.12 (s, 3H), 1.59 (s, OH), 1.98 (m, 1H), 2.11–2.31 (m, 2H), 2.53 (m, 1H). ^{13}C NMR ($CDCl_3$): δ=12.5, 17.0, 24.9, 36.0, 36.8, 39.8, 76.4, 218.1.

4.4.2. 1-Butyl-2-methyl-5-vinylcyclopent-2-enol (5a). (Oil, 10%) ^{1}H NMR ($CDCl_3$): δ=0.82 (t, J=6.7 Hz, 3H), 1.23 (s, 3H), 1.35–2.45 (m, 10H), 4.99–5.08 (m, 2H), 6.54 (m, 1H). ^{13}C NMR ($CDCl_3$): δ=13.9, 23.3, 24.5, 25.9, 27.9, 33.1, 39.6, 85.2, 114.7, 131.6, 135.5, 146.0.

4.4.3. (*Z* and *E*)-6-But-3-enyl-2-methyl-7-oxabicyclo-[4.1.0]heptane (4b). *tert*-Butyllithium (0.1 M in THF) was used as base in this case (oil, 61%). The product that results from S_N2 prime nucleophilic attack was obtained as a mixture of *Z* and *E* diastereomers. ^{1}H NMR ($CDCl_3$): δ=0.87 (s, 9H), 0.89 (s, 9H), 1.37 (s, 2×3H), 1.40–1.78 (m, 2×3H), 1.94 (m, 2×2H), 2.08 (m, 2×1H), 2.15 (m, 2×1H), 2.27 (m, 2×1H), 3.19 (s, 1H), 3.46 (s, 1H), 5.65 (m, 2×1H). ^{13}C NMR ($CDCl_3$): δ=18.8, 20.3, 23.2, 23.6, 29, 3 (2C), 29.5, 30.0, 30.3, 30.7, 31.3, 31.6, 40.7, 41.7, 57.5 (2C), 64.4 (2C), 129.9, 130.3, 133.7, 133.8.

4.4.4. 5-Methoxy-2-methyl-tricyclo[6.1.0.0.3.4]nonan-2-ol (4d). (Oil, 47%) ^{1}H NMR ($CDCl_3$): δ=0.73 (m, 2H), 0.90 (s, 3H), 1.05 (m, 1H), 1.33–1.45 (m, 2H), 1.63–1.76 (m, 3H), 1.87 (m, 1H), 2.02 (m, 1H), 2.15 (m, 1H), 3.02 (brs, 1H), 3.16 (s, 3H). ^{13}C NMR ($CDCl_3$): δ=7.9, 22.1, 22.7, 25.4, 29.9, 30.1, 40.8, 46.6, 51.8, 78.5, 95.0. HRMS calcd for $C_{10}H_{15}O_2$ (M^+−Me) 167.1072; found 167.1089.

4.4.5. 3-But-3-enyl-2-butyl-1-methylcyclopent-2-enol (5d). (Oil, 26%) ^{1}H NMR ($CDCl_3$): δ=0.83 (t, J=7 Hz, 3H), 1.23 (s, 3H), 1.28–1.39 (m, 4H), 1.75–2.07 (m, 9H), 2.22 (m, 1H), 4.84–4.97 (m, 2H), 5.76 (m, 1H). ^{13}C NMR ($CDCl_3$): δ=14.0, 23.4, 24.5, 26.0, 28.4, 31.2, 32.1, 32.9, 40.1, 85.4, 114.5, 138.2, 138.5, 141.0.

4.4.6. 6-Methoxytricyclo[7.1.0.0.3.5]decan-2-ol (4e). (Oil, 37%) ^{1}H NMR ($CDCl_3$): δ=0.23 (m, 2H), 0.80 (ddd, J=4, 7.2, 11.2 Hz, 1H), 1.23 (m, 2H), 1.58 (m, 1H), 1.61–1.75 (m, 4H), 1.77–1.93 (m, 3H), 3.14 (s, 3H), 3.40 (dt, J=2.7, 9.2 Hz, 1H), 4.75 (d, J=9.2 Hz, OH). ^{13}C NMR ($CDCl_3$): δ=6.5, 13.7, 18.5, 20.7, 25.1, 26.4, 28.7, 32.9, 51.7, 73.8, 91.5. HRMS calcd for $C_{10}H_{15}O_2$ (M^+−Me) 167.1072; found 167.1072.

4.4.7. 6-But-3-enyl-1-butylcyclohex-2-enol (5e). (Oil, 46%) ^{1}H NMR ($CDCl_3$): δ=0.83 (t, J=6.8 Hz, 3H), 1.21–1.35 (m, 5H), 1.54–1.71 (m, 4H), 1.89 (m, 1H), 1.95–2.12 (m, 6H), 3.98 (brs, 1H), 4.85–4.97 (m, 2H), 5.74 (m, 1H). ^{13}C NMR ($CDCl_3$): δ=14.1, 17.9, 23.1, 29.5, 29.7, 31.7, 32.1, 32.5, 32.6, 67.1, 114.4, 133.2, 134.7, 138.6. HRMS calcd for $C_{14}H_{24}O$ (M^+) 208.1827; found 208.1816.

4.4.8. (*cis*)-6-But-3-enyl-5-methoxy-2-methyl-bicyclo[3.1.0]hexan-2-ol (4f). (Oil, 24%) ^{1}H NMR ($CDCl_3$): δ=0.63 (m, 1H), 1.02 (d, J=3 Hz, 1H), 1.10 (m, 1H), 1.16 (s, 3H), 1.34 (m, 1H), 1.50–1.61 (m, 2H), 1.84 (dd, J=8, 12 Hz, 1H), 2.07–2.16 (m, 2H), 2.18 (m, 1H), 3.28 (s, 3H), 4.86–4.99 (m, 2H), 5.76 (m, 1H). ^{13}C NMR ($CDCl_3$): δ=25.1, 25.8, 27.2, 27.5, 33.9, 37.0, 39.8, 55.8, 73.3, 79.2, 114.7, 138.7.

4.4.9. (*trans*)-6-But-3-enyl-5-methoxy-2-methyl-bicyclo[3.1.0]hexan-2-ol (4f'). (Oil, 33%) ^{1}H NMR ($CDCl_3$): δ=1.20 (s, 3H), 1.23–1.55 (m, 5H), 1.84 (m, 1H), 2.02 (dd, J=7.8, 12.2 Hz, 1H), 2.18 (m, 2H), 2.32 (m, 1H), 3.30 (s, 3H), 4.97–5.08 (m, 2H), 5.85 (m, 1H). ^{13}C NMR ($CDCl_3$): δ=23.2, 25.7, 26.0, 28.7, 34.8, 39.8, 39.9, 55.4, 73.5, 79.2, 115.0, 138.7.

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