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# REARRANGEMENT OF EPOXIDE DERIVATIVES SEMISYNTHESIZED FROM β-HIMACHALENE USING LEWIS AND BRONSTED ACIDS CATALYSIS

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*The acid-catalyzed rearrangement of epoxides **3a**, **4a**, **6a**, and **7a** derived from* β*-himachalene, the major constituent of* Cedrus atlantica *essential oil, has been studied using various Lewis and Bronsted acids. Several new enantiomerically pure ketones were obtained in good yields and high selectivities. All products obtained were fully characterized by* $^{1}H$ *and* $^{13}C$ *NMR, and the mechanistic explanations for their formation were proposed.*

**Keywords**: β-himachalene, epoxidation, Meinwald rearrangement, acid catalysis.

In recent years, natural substances have attracted growing interest in several industrial fields [1–3], including the cosmetic, pharmaceutical, and food industries. In addition, valorization of active ingredients of natural origin represents high added value from the economic point of view. In this context, modern pharmaceutical industry still relies heavily on the diversity of plant secondary metabolites in order to find new molecules with interesting biological properties [4].

With regard to its special geographical position, Morocco possesses varied vegetation and is considered among the top five floristically richest countries across the Mediterranean basin [5]. These natural resources include *Cedrus atlantica* essential oil, which is considered as a valuable starting material for the perfume industry. This oil is primarily made up of sesquiterpenic bicyclic hydrocarbons (75%), in which β-himachalene represents the major component [6, 7]. The reactivity of this sesquiterpene and its derivatives has been studied extensively in order to prepare new products having enhanced biological activities [8–10].

Previous studies have shown that the acid-catalyzed rearrangement of two enantiomerically pure epoxides 2α,3α-epoxy-*cis*-himachal-7(13)-ene and 6α,7α-epoxyhimachal-2-ene derived from α-*cis* and β-himachalene, respectively, gave several new polycyclic compounds with different selectivities depending upon the catalysts used and the reaction conditions [11, 12].

In addition, the rearrangement of epoxides to carbonyl compounds represents a useful synthetic transformation and hence several products could be obtained according to the nature of the epoxide, catalysts, and reaction conditions [13]. A large number of catalyst types have been used in the literature for this purpose, including a variety of Lewis acids [14, 15].

Within the framework of a research project based on valorization of Moroccan plant resources [16–20], we herein report the synthesis of a new epoxide himachalenes skeleton starting from β-himachalene [21, 22] isolated from *Cedrus atlantica* essential oil using chromatography on a silica gel column impregnated with silver nitrate (10%) and a mixture of hexane–ethyl acetate (99:1) as eluent. We decided to explore the chemistry of gem-dihalogenocyclopropane oxides **3a**, **4a**, **6a**, and **7a** (Scheme 1). The rearrangements of these epoxides to the corresponding carbonyl compounds were studied with different Lewis and Bronsted acids.

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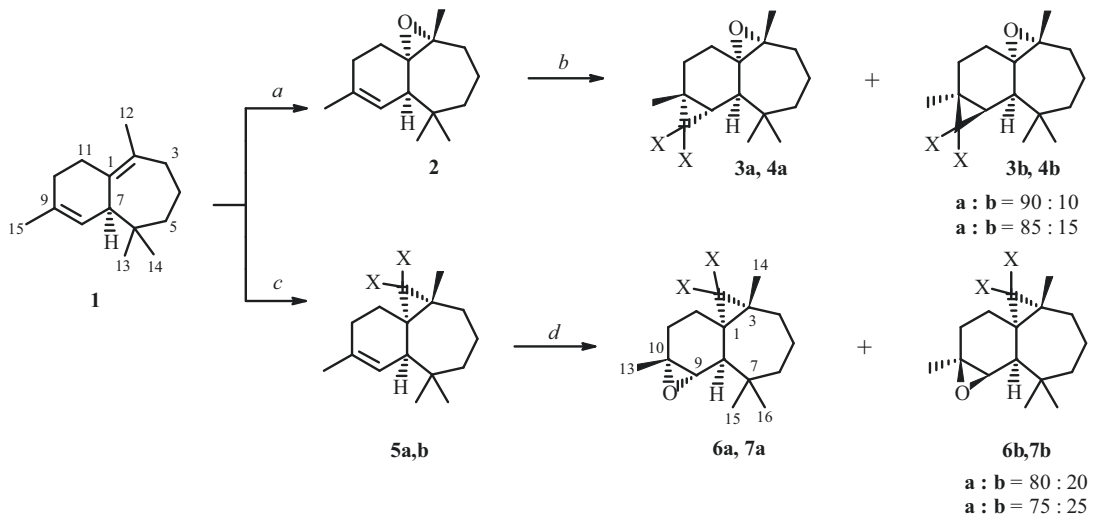



**5a:** X = Br; **5b:** X = Cl; **3, 6:** X = Br (63%); **4, 7:** X = Cl (83%)

*a*. *m*-CPBA (1 eq.), $CH_2Cl_2$, r.t.; *b*. $CHX_3$, *t*-BuOK (1.5 eq.); *c*. $CHX_3$, *t*-BuOK (1 eq); *d*. *m*-CPBA (1.5 eq.), $CH_2Cl_2$, r.t.

Scheme 1. General pathway for the synthesis of gem-dihalogenocyclopropane oxides **3a**, **4a**, **6a**, and **7a**.

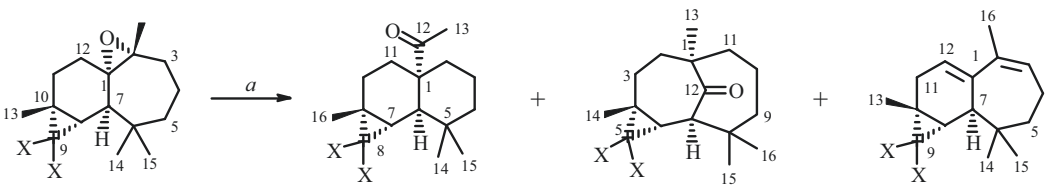
We investigated the rearrangement of the epoxides derived from *β*-himachalene. The epoxides were synthesized as described in the literature [23, 24]. Firstly, the *β*-himachalene was transformed to the corresponding epoxides using m-CPBA (1 eq) in dichloromethane. The products **3** and **4** were obtained with yields of 63 and 83%, respectively, as two diastereoisomers (Scheme 1) from *β*-epoxyhimachalene by the action of chloroform or bromoform (1.5 eq) in the presence of potassium *tert*-butylate (*t*-BuOK) as a base in hexane.

Using the same strategy, we prepared other epoxides from *β*-himachalene. Indeed, *β*-himachalene was converted to the corresponding dihalogenocyclopropanes under the same conditions previously described but using only 1 eq of chloroform (or bromoform). The reaction allowed us to obtain products **5a** and **5b** with yield of 10 and 55%, respectively, after 15 h of stirring at room temperature. In both cases, the reaction gave regio- and stereospecifically one enantiomer [23, 25]. Then the epoxidation of the products **5a** and **5b** was carried out and led to the products **6** and **7** with yields of 63 and 83% as two diastereoisomers with a–b ratios of 80:20 and 75:25, respectively (Scheme 1). In all cases the majority of epoxides were isolated and purified using chromatography on a silica gel column and a mixture of hexane–ethyl acetate (99:1) as eluent. The structures of all obtained products were established by $^1H$ and $^{13}C$ NMR. The stereochemistry of the asymmetric carbons was confirmed by single-crystal X-ray diffraction [26, 27].

We have shown previously that Lewis acids are efficient catalysts for epoxide opening-mediated rearrangement [11, 12]. Our study began with the epoxides **3a** and **4a**, which were treated using $BF_3$–$Et_2O$ (0.1%) in dichloromethane. This led predominantly to the formation of two tricyclic ketones (**8a**, **8b**) and (**9a**, **9b**), respectively (Scheme 2).

A full conversion was obtained after 0.5 h and led to the formation of ketones **8a** and **8b** as major products. The structures of the newly prepared products were characterized by their spectral data (NMR). Then we investigated the effect of different Lewis and Bronsted acids on the conversion and selectivity of the reaction. The results obtained are summarized in Table 1.

In all cases (E1-E7), complete conversion was obtained, and the selectivity depended on the nature of the acid. The rearrangement products were obtained with high selectivity to total carbonylated products ranging from 50 (E6) to 96% (E1).



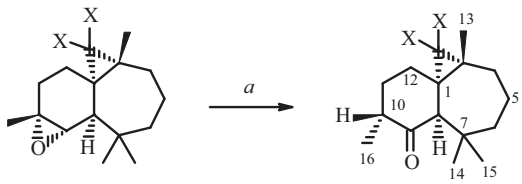

**8a, 9a, 10a:** X = Br; **8b, 9b, 10b:** X = Cl

*a*. Lewis acid, $CH_2Cl_2$

Scheme 2. Rearrangement of products **3a** and **4a**.

TABLE 1. Rearrangement of Epoxides **3a** and **4a** Catalyzed with 0.1% of Acids

| Entry (E) | Compound | Catalyst | Time, min | Product yield | | | |
|---|---|---|---|---|---|---|---|
| | | | | **8** | **9** | **10** | **11** |
| 1 | **3a** | $BF_3$–$OEt_2$ | 30 | 88 | 8 | 2 | |
| 2 | | $InCl_3$ | 120 | 87 | 2 | 4 | |
| 3 | | $Bi(OTf)_3$ | 20 | 76 | 6 | 0 | |
| 4 | | $SnCl_2$–$2H_2O$ | 240 | 82 | 7 | 3 | |
| 5 | | $Sn(OTf)_2$ | 45 | 65 | 10 | 0 | |
| 6 | | $FeCl_3$–$6H_2O$ | 120 | 50 | 0 | 2 | |
| 7 | | $AlCl_3$ | 120 | 55 | 17 | 0 | |
| 8 | | PTSA | 30 | 0 | 0 | 92 | |
| 9 | | MSA | 30 | 0 | 0 | 90 | |
| 10 | **4a** | $BF_3$–$OEt_2$ | 30 | 91 | 0 | 5 | |
| 11 | | $InCl_3$ | 90 | 87 | 0 | 8 | |
| 12 | | $Bi(OTf)_3$ | 20 | 89 | 0 | 9 | |
| 13 | **6a** | $BF_3$–$OEt_2$ | 120 | | | | 93 |
| 14 | | $InCl_3$ | 240 | | | | 92 |
| 15 | | $Bi(OTf)_3$ | 90 | | | | 90 |
| 16 | **7a** | $BF_3$–$OEt_2$ | 120 | | | | 90 |
| 17 | | $InCl_3$ | 240 | | | | 88 |
| 18 | | $Bi(OTf)_3$ | 90 | | | | 92 |




**6a, 7a** **11a,b**

**6a, 11a:** X = Br; **7a, 11b:** X = Cl

*a*. Lewis acid, $CH_2Cl_2$

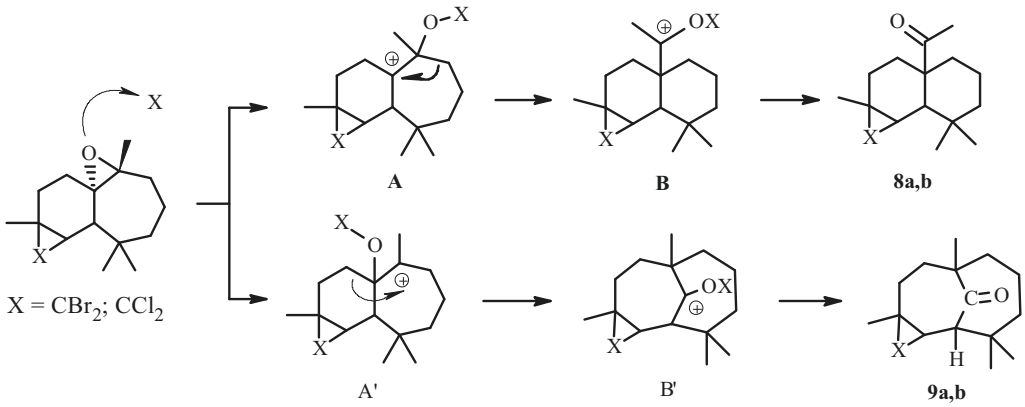
Scheme 3. Ring opening reaction of **6a** and **7a.**

Comparison of the various tests showed the remarkable effect of the Lewis acid on the rate and selectivity of the reaction. With $BF_3$–$OEt_2$, $Bi(OTf)_3$, and $Sn(OTf)_2$, a complete and rapid conversion of epoxide was observed (E1, E3, and E5), while the reaction time must be increased to 2 or 4 h to obtain a complete conversion of the substrate with $InCl_3$, $FeCl_3$, and $AlCl_3$ (E2, E6, and E7). Indeed, $BF_3$–$OEt_2$ catalyst gave the best selectivity to carbonylated products with excellent chemoselectivity (96%) and a selectivity of **8a** and **9a** (E1) of 88% and 8%, respectively. However a middle chemoselectivity was obtained using $Sn(OTf)_2$, $FeCl_3$–$6H_2O$ or $AlCl_3$.

Bronsted acids have been used as catalysts in order to compare their activities and selectivities to those of Lewis acids. The reaction was studied under the same conditions with methanesulfonic acid (MSA) and *p*-toluenesulfonic acid (PTSA). In both cases no traces of ketones or alcohols were observed, and only side products due to dehydration and isomerization of the double bonds formed were detected by gas chromatography. We were able to get the product **10a** with a selectivity of 92% using PTSA (E8) and 90% with MSA (E9).

Following the encouraging results obtained with epoxide **3a** and Lewis acid in terms of selectivity, we decided to extend this reaction to other epoxides. The chlorinated analogous **4a** gave similar results as those obtained previously in terms of conversion, with total chemoselectivity to the ketone **8b** (87–91%) (E10–E12), since no trace of the ketone **9b** was detected. We also noticed a slight improvement in the chemoselectivity for carbonyl products with the catalysts tested ($BF_3$–$OEt_2$, $Bi(OTf)_3$, and $InCl_3$). A selectivity of 91% was recorded with $BF_3$–$OEt_2$ (E10).

To that end, the ring-opening reaction of epoxides **6a** and **7a** was investigated under the same catalytic conditions (Scheme 3). The results obtained are summarized in Table 1.




Scheme 4. Proposed mechanism of epoxide-opening rearrangement using Lewis acid catalysts.

The reaction led predominantly to the formation of the corresponding ketones with good yields ranging from 88% to 93% (E13–E18), and $BF_3$–$OEt_2$ proved to be the best catalyst for the opening of these epoxides 93% (E13). The gas chromatography of the reaction mixture revealed the presence of other easily identifiable products in very small quantities up to 12%.

The structures of the newly prepared ketones were established by $^1H$ and $^{13}C$ NMR after purification on a silica gel column. In addition, all products were crystallized using slow diffusion in pentane at room temperature. The molecular structures and relative stereochemistry of compounds **8a**, **8b**, **9a**, **9b**, **11a**, and **11b** were elucidaed unambiguously by single-crystsl X-ray diffraction [28–32].

In order to explain the formation of these compounds, we proposed the mechanism presented in Scheme 4, based on previous work reported by Meinwald and co-workers [15]. The formation of the products can be explained by the transfer of the free electron pair from the epoxide oxygen to the orbital empty catalyst, which promoted the formation of two carbocations A and A′. The product **8** was obtained by the rearrangement of carbocation A via the opening of the C2–C3 bond and migration of C3 to C1. Moreover, the rearrangement of the carbocation A′ was carried out by the migration of C12 to C2 and led to the formation of product **9** (Scheme 4).

In this work, we have described an efficient opening of epoxides **3a**, **4a**, **6a**, and **7a** semisynthesized from *β*-himachalene, the main component of *Cedrus atlantica* essential oil, using Lewis acid catalysts, into enantiomerically pure corresponding ketones in good yields and high selectivities.

The high catalytic activities and chemoselectivities in favor of carbonyl compounds can be achieved using Lewis acids, more particularly with $BF_3$–$OEt_2$, which gave the best result with different epoxides. However, using Bronsted acids led selectively to the formation of dehydration products. Further studies, including the biological activities of the ketones obtained, are currently in progress.

In summary, the epoxy himachalene scaffolds **3a**, **4a**, **6a**, and **7a** appear to be an interesting source of new chiral polycyclic structures, which can be valuable intermediates in the agrochemical and pharmaceutical industries.

## EXPERIMENTAL

**General**. All operations were carried out in an inert atmosphere of nitrogen gas using technical standard check. Column chromatography was performed using 70–230 mesh silica gel. All reagents and solvents were obtained from commercial suppliers and used without further purification. All compounds were characterized by $^1H$ and $^{13}C$ NMR. All NMR spectral data were recorded at 25°C on DPX300 spectrometers with TMS as internal for $^1H$ and $^{13}C$. Spectral assignments were made by means of routine one- and two-dimensional NMR experiments where appropriate. Melting points were taken on a Buchi 510 capillary apparatus. Mass spectra (MS) were recorded on GC/TOF using chemical ionization by desorption in methane.

**General Procedure of Epoxidation**. To a solution of compound **5a** (500 mg, 1.33 mmol) in $CH_2Cl_2$ (20 mL) was added *m*-CPBA (241 mg, 2 mmol) portion wise at 0°C. The mixture was stirred at room temperature for 2 h. Then it was diluted with $CH_2Cl_2$ (20 mL) and washed twice with a solution of 10% $NaHCO_3$ (20 mL). The organic phase was combined and washed twice with 20 mL of distilled water, dried over $Na_2SO_4$, filtered, and concentrated under vacuum. The crude material was purified by silica gel CC using *n*-hexane–EtOAc (98:2) as eluent.

**For the gem-dihalogenocyclopropanation reaction procedure,** see [9 and 23].

**(1*S*,3*R*,8*R*,9*S*,10*R*)-2,2-Dibromo-9,10-epoxy-3,7,7,10-tetramethyltricyclo[6.4.0.0$^{1,3}$]dodecane (6a)**, white powder, mp 126–127°C. $^1$H NMR (300 MHz, $CDCl_3$, δ, ppm, J/Hz): 0.88, 0.89 (each 3H, s, H-15, 16), 1.04 (3H, s, H-14), 1.05–1.70 (10H, m, H-4, 5, 6, 11, 12), 1.14 (1H, d, J = 3.3, H-8), 1.20 (3H, s, H-13), 3.04 (1H, d, J = 3.3, H-9). $^{13}$C NMR (75 MHz, $CDCl_3$, δ, ppm): 39.2 (C-1), 47.3 (C-2), 33.1 (C-3), 35.6 (C-4), 19.5 (C-5), 41.1 (C-6), 27.3 (C-7), 42.5 (C-8), 70.5 (C-9), 62.3 (C-10), 24.6 (C-11), 24.8 (C-12), 23.5 (C-13), 18.2 (C-14), 27.4 (C-15), 27.6 (C-16). MS *m/z* 391.8 $[M]^+$.

**(1*S*,3*R*,8*R*,9*S*,10*R*)-2,2-Dichloro-9,10-epoxy-3,7,7,10-tetramethyltricyclo[6.4.0.0$^{1,3}$]dodecane (7a)**, white powder, mp 136–137°C. $^1$H NMR (300 MHz, $CDCl_3$, δ, ppm, J/Hz): 1.05–1.71 (10H, m, H-4, 5, 6, 11, 12), 3.01 (1H, d, J = 3.3, H-9), 1.12 (1H, d, J = 3.3, H-8), 1.22 (3H, s, H-14), 1.35 (3H, s, H-13), 1.04, 1.09 (each 3H, s, H-15, H-16). $^{13}$C NMR (75 MHz, $CDCl_3$, δ, ppm): 39.1 (C-1), 76.15 (C-2), 33.4 (C-3), 35.8 (C-4), 19.3 (C-5), 41.4 (C-6), 27.1 (C-7), 42.3 (C-8), 54.8 (C-9), 60.9 (C-10), 24.3 (C-11), 24.7 (C-12), 23.3 (C-13), 18.1 (C-14), 27.3 (C-15), 27.7 (C-16). MS *m/z* 303 $[M]^+$.

**General Procedure for the Rearrangement Reaction of Epoxide Derivatives.** Epoxide (5 mmol) was dissolved in $CH_2Cl_2$ (10 mL) and stirred at room temperature under argon. Then 1% mmol of Lewis acid (or Bonsted acid) was added to the solution, and the reaction mixture was stirred and monitored by TLC. After completion of the reaction, the reaction mixture was diluted with 10 mL of $CH_2Cl_2$ and washed using saturated aqueous solutions of $NaHCO_3$ (10 mL). The organic layer was dried with sodium sulfate ($Na_2SO_4$), and the solvent was removed on a rotary evaporator. The reaction mixture was analyzed by gas chromatography and then purified using flash column chromatography.

**Ring Opening of Epoxide with $BF_3$–$OEt_2$**. $BF_3$–$OEt_2$ (0.2 mL) was added dropwise to a solution of epoxide (0.66 mol) in $CH_2Cl_2$ (20 ml) at –78°C under $N_2$. The reaction mixture was stirred for 90 min at constant temperature and then left at room temperature for 24 h. Water (20 mL) was added in order to separate the two phases, and the organic phase was dried and concentrated. Silica-gel chromatography of the crude gave the ketone in a yield of 60%. Crystallization was carried out at room temperature from a hexane solution.

**1-[(1*S*,6*R*,7*S*,9*R*)-8,8-Dibromo-5,5,9-trimethyltricyclo[5.4.0.0$^{7,9}$]undecan-1-yl]ethanone (8a)**, white powder, mp 74–76°C. $^1$H NMR (300 MHz, $CDCl_3$, δ, ppm, J/Hz): 0.85, 0.98 (each 3H, s, H-14, 15), 1.31–2.02 (10H, m, H-2, 3, 4, 10, 11), 1.44 (3H, s, H-16), 1.88 (1H, d, J = 3, H-6), 1.98 (1H, d, J = 3, H-7), 2.13 (3H, s, H-13). $^{13}$C NMR (75 MHz, $CDCl_3$, δ, ppm): 52.8 (C-1), 35.5 (C-2), 16.5 (C-3), 44.7 (C-4), 29.4 (C-5), 62.2 (C-6), 36.7 (C-7), 49.0 (C-8), 35.1 (C-9), 29.4 (C-10), 25.5 (C-11), 212.7 (C-12), 25.0 (C-13), 18.1 (C-14), 19.2 (C-15), 17.0 (C-16). MS *m/z* 392 $[M]^+$.

**1-[(1*S*,6*R*,7*S*,9*R*)-8,8-Dichloro-5,5,9-trimethyltricyclo[5.4.0.0$^{7,9}$]undecan-1-yl]ethanone (8b),** white powder, mp 54–56°C. $^1$H NMR (300 MHz, $CDCl_3$, δ, ppm, J/Hz): 0.85, 0.98 (each 3H, s, H-14, 15), 1.31–2.02 (10H, m, H-2, 3, 4, 10, 11), 1.40 (3H, s, H-16), 1.85 (1H, d, J = 3, H-6), 1.97 (1H, d, J = 3, H-7), 2.12 (3H, s, H-13). $^{13}$C NMR (75 MHz, $CDCl_3$, δ, ppm): 49.0 (C-1), 35.1 (C-2), 18.5 (C-3), 44.7 (C-4), 29.4 (C-5), 52.8 (C-6), 36.7 (C-7), 72.3 (C-8), 35.5 (C-9), 29.4 (C-10), 25.7 (C-11), 212.7 (C-12), 25.0 (C-13), 18.2 (C-14), 19.1 (C-15), 17.4 (C-16). MS *m/z* 302 $[M]^+$.

**(1*R*,4*R*,6*S*,7*R*)-5,5-Dibromo-1,4,8,8-tetramethyltricyclo[5.4.1$^{1,7}$.0$^{4,6}$]dodecan-12-one (9a),** white powder, mp 79–80°C. $^1$H NMR (300 MHz, $CDCl_3$, δ, ppm, J/Hz): 0.90, 1.1 (each 3H, s, H-15, 16), 1.23–1.81 (10H, m, H-2, 3, 9, 10, 11), 1.38 (3H, s, H-14), 1.44 (3H, s, H-13), 1.80 (1H, d, J = 13, H-6), 2.10 (1H, d, J = 13, H-7). $^{13}$C NMR (75 MHz, $CDCl_3$, δ, ppm): 46.9 (C-1), 26.2 (C-2), 37.3 (C-3), 30.1 (C-4), 43.9 (C-5), 35.4 (C-6), 51.8 (C-7), 30.0 (C-8), 48.1 (C-9), 20.2 (C-10), 36.2 (C-11), 219.1 (C-12), 19.0 (C-13), 17.5 (C-14), 22.3 (C-15), 21.9 (C-16). MS *m/z* 392 $[M]^+$.

**(1*R*,4*R*,6*S*,7*R*)-5,5-Dichloro-1,4,8,8-tetramethyltricyclo[5.4.1$^{1,7}$.0$^{4,6}$]dodecan-12-one(9b)**, white powder, mp 61–62°C. $^1$H NMR (300 MHz, $CDCl_3$, δ, ppm, J/Hz): 0.91, 1.12 (each 3H, s, H-15, 16), 1.14 (3H, s, H-14), 1.21–1.83 (10H, m, H-2, 3, 9, 10, 11), 1.42 (3H, s, H-13), 1.7 (1H, d, J = 13, H-6), 2.20 (1H, d, J = 13, H-7). $^{13}$C NMR (75 MHz, $CDCl_3$, δ, ppm): 46.7 (C-1), 26.3 (C-2), 37.1 (C-3), 30.3 (C-4), 43.7 (C-5), 35.1 (C-6), 51.6 (C-7), 29.8 (C-8), 48.3 (C-9), 20.4 (C-10), 36.1 (C-11), 215.5 (C-12), 19.2 (C-13), 17.3 (C-14), 22.1 (C-15), 21.8 (C-16). MS *m/z* 303.25 $[M]^+$.

**(7*R*,8*S*,10*R*)-9,9-Dibromo-2,6,6,10-tetramethyltricyclo[5.5.0.0$^{2,4}$]dodeca-1,2-diene (10a)**, white powder, mp 121–122°C. $^1$H NMR (300 MHz, $CDCl_3$, δ, ppm, J/Hz): 0.82, 1.05 (each 3H, s, H-14, 15), 0.97–1.36 (6H, m, H-4, 5, 11), 1.04 (3H, s, H-13), 1.05 (1H, d, J = 3, H-8), 1.91 (1H, d, J = 3, H-7), 2.01 (3H, s, H-16), 5.5 (2H, m, H-3, 12). $^{13}$C NMR (75 MHz, $CDCl_3$, δ, ppm): 137.06 (C-1), 137.3 (C-2), 124.62 (C-3), 45.55 (C-4), 29.61 (C-5), 42.7 (C-6), 50.5 (C-7), 36.52 (C-8), 60.05 (C-9), 45.55 (C-10), 35.01 (C-11), 127.38 (C-12), 27.86 (C-13), 28.46 (C-14), 23.52 (C-15), 24.47 (C-16). MS *m/z* 374 $[M]^+$.

**(7*R*,8*S*,10*R*)-9,9-Dichloro-2,6,6,10-tetramethyltricyclo[5.5.0.0$^{2,4}$]dodeca-1,2-diene (10b)**, white powder, mp 101–103°C. $^1$H NMR (300 MHz, $CDCl_3$, δ, ppm, J/Hz): 0.82, 1.06 (each 3H, s, H-14, 15), 0.96–1.37 (6H, m, H-4, 5, 11), 1.04 (1H, d, J = 3, H-8), 1.05 (3H, s, H-13), 1.90 (1H, d, J = 3, H-7), 2.01 (3H, s, H-16), 5.40 (2H, m, H-3, 12). $^{13}$C NMR

(75 MHz, $CDCl_3$, δ, ppm): 135.07 (C-1), 136.8 (C-2), 124.64 (C-3), 45.55 (C-4), 29.42 (C-5), 42.70 (C-6), 50.06 (C-7), 35.01 (C-8), 73.5 (C-9), 45.57 (C-10), 36.52 (C-11), 126.9 (C-12), 27.86 (C-13), 28.32 (C-14), 23.52 (C-15), 24.47 (C-16). MS *m/z* 284 $[M]^+$.

**(1*S*,3*R*,8*R*,10*R*)-2,2-Dibromo-3,7,7,10-tetramethyltricyclo[6.4.0.0$^{1,3}$]dodecan-9-one (11a)**, white powder, mp 91–93°C. $^1H$ NMR (300 MHz, $CDCl_3$, δ, ppm, J/Hz): 0.92 (3H, d, J = 3, H-16), 1.09 (6H, s, H-14, 15), 1.10 (3H, d, J = 12, H-13), 1.22–2.10 (10H, m, H-4, 5, 6, 11, 12), 2.30–2.40 (1H, m, H-10), 2.40 (1H, s, H-8). $^{13}C$ NMR (75 MHz, $CDCl_3$, δ, ppm): 45.88 (C-1), 59.06 (C-2), 34.95 (C-3), 35.98 (C-4), 16.16 (C-5), 45.93 (C-6), 31.68 (C-7), 75.86 (C-8), 209.11 (C-9), 46.50 (C-10), 29.93 (C-11), 33.01 (C-12), 20.74 (C-13, 14), 21.40 (C-14, 15), 27.01 (C-15), 15.95 (C-16, 13). MS *m/z* 392 $[M]^+$.

**(1*S*,3*R*,8*R*,10*R*)-2,2-Dichloro-3,7,7,10-tetramethyltricyclo[6.4.0.0$^{1,3}$]dodecan-9-one (11b)**, white powder, mp 89–90°C. $^1H$ NMR (300 MHz, $CDCl_3$, δ, ppm, J/Hz): 1.09 (3H, d, J = 3, H-16), 1.10 (3H, d, J = 12, H-13), 1.22 (6H, s, H-14, 15), 1.56–2.20 (10H, m, H-4, 5, 6, 11, 12), 2.45 (1H, m, H-10), 2.65 (1H, s, H-8). $^{13}C$ NMR (75 MHz, $CDCl_3$, δ, ppm): 34.8 (C-1), 76.9 (C-2), 32.1 (C-3), 31.0 (C-4), 25.2 (C-5), 43.8 (C-6), 28.8 (C-7), 45.0 (C-8), 213.0 (C-9), 38.3 (C-10), 27.2 (C-11), 25.2 (C-12), 15.4 (C-13), 26.4 (C-14), 26.2 (C-15), 20.5 (C-16). MS *m/z* 302 $[M]^+$.

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