Tetrahedron: *Asymmetry* 27 (2016) 698–705

Contents lists available at ScienceDirect

Tetrahedron: *Asymmetry*

journal homepage: www.elsevier.com/locate/tetasy

BINOL-Al catalyzed kinetic resolution of citronellal analogues: synthesis of a variety of fragrances

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ARTICLE INFO

Article history:
Received 7 April 2016
Accepted 5 June 2016
Available online 23 June 2016

ABSTRACT

A chiral aluminum catalyst was used for the kinetic resolution of citronellal analogues. Racemic 3-alkylcitronellals gave optically active 5-alkylisopulegols with high enantioselectivity. Unreacted 3-alkylcitronellal analogues were obtained with low enantioselectivity. The two main diastereoisomers of the product were opposite to each other. The scents of 5-substituted isopulegols were evaluated. The chiral recognition of the catalysts and their effects on the kinetic resolutions are also discussed.

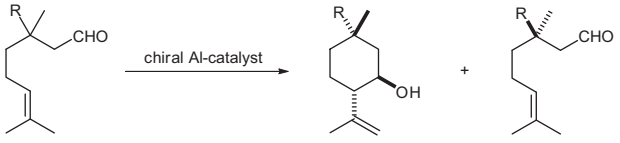
1. Introduction

In the field study of organic synthesis, optically active products are widely desired for the preparation of organic materials, aroma chemicals and intermediates for medicine. A number of asymmetric intermolecular or intramolecular ene reactions have been studied in order to provide practical synthetic methods for optically active products. Ene and Prins reactions between carbonyl and olefin groups have been reported.[1] The intramolecular Prins reaction is often a key reaction in the synthesis of natural products. Overman et al. reported a Briarellin F synthesis using a Prins reaction.[1d] Kopecky and Rychnovsky reported the synthesis of Leucascandrolide A via a Mukaiyama aldol–Prins cyclization cascade reaction.[1e,f] Recently, Zhenlei et al. presented total synthesis of (−)-exiguolide with Prins cyclization as a key strategy.[2] Lalli et al. researched a novel aza-Prins cyclization promoted by a synergistic combination between a Lewis acid and a Bronsted acid to afford piperidine.[3]

The kinetic resolution of racemic compounds is an important method of asymmetric synthesis. An enormous number of kinetic resolutions by enzymes or biocatalysts have been studied.[4] Asymmetric reactions utilizing kinetic resolutions by low temperature have also been reported.[5] Kinetic resolutions with organic and organometallic catalyst have been studied in recent years.[6] Kagan et al. found a variety of kinetic resolutions and opened up a modern study of kinetic resolution.[7] In recent articles, Aoyama et al. reported on excellent enantioselective alcoholysis by the kinetic resolution.[8] Lu et al. researched the kinetic resolution of racemic 5-alkylcyclohexenones via Pd catalyzed 1,4-additions of arylboronic acids.[9] A silylation-based kinetic resolution of secondary alcohols with a polystyrene-supported triphenylsilyl chloride was reported by Wiskur et al.[10a] Wiskur et al. also presented the silylation-based kinetic resolution of α-hydroxy lactones and lactams,[10b] and linear free-energy relationship and rate studies on a silylation-based kinetic resolution.[10c] Salvio et al. reported a kinetic resolution of phosphoric diester by cinchona alkaloid derivatives.[11]

These kinetic resolutions are mainly hydrolysis, reduction, oxidation and ring-opening reactions, and other substituent changing reactions.[12] As an example of a ring-closing kinetic resolution, Hoveyda and Schrock investigated the kinetic resolution of chiral dienes by a chiral molybdenum catalyst.[13]

We previously reported on the kinetic resolution of racemic citronellal with a variety of aluminum catalysts bearing chiral ligands.[14] The resolution was successfully preformed and afforded optically active isopulegol and citronellal. Herein, we utilize a chiral aluminum catalyst in the kinetic resolution of other substrates (Scheme 1). The details of the resolution and the differences between those of racemic citronellal are also investigated.



Scheme 1. Kinetic resolution of citronellal analogues.

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http://dx.doi.org/10.1016/j.tetasy.2016.06.007
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2. Results and discussion

At first, a variety of ligands were utilized for the kinetic resolution and the results are shown in Table 1. The chiral ligands are shown in Figure 1. The kinetic resolution of the racemic citronellal analogue 3-vinylcitronellal (±)-**1**[15,16] with chiral aluminium catalysts bearing (*R*)-BINOL (*R*)-**L1a** was successfully carried out (entry 1). The conversion was calculated as the total consumption of a substrate. 3-Vinylcitronellal (±)-**1** gave 5-vinylisopulegols **2** and unreacted **1**. The diastereoisomers of **2** were mainly *anti*-**2** (1α,2β,5β-**2**) and *syn*-**2** (1α,2β,5α-**2**). The diastereoselectivity of *anti*-**2** was 68% at 46% conversion, lower than that obtained with citronellal.[14] Other possible isomers were barely detected by GC. The absolute configurations of **2** were determined with an advanced Mosher method.[17] The *ee* of *anti*-**2** was 71%. The *ee* of *syn*-**2** reached 89%. By contrast, the *ee* of (−)-**1** was 25%. The k_{rel}[18] of this resolution was 2.3 at 46% conversion.

Catalysts with (*R*)-**L1a** and (*S*)-**L1a** ligands showed almost the same performance except with regards to the specific rotation (entries 1 and 2). The reaction with (*S*)-**L1a** afforded (−)-**2** and left (+)-**1**. The ratio of *anti*-**2**/*syn*-**2** was 68/32 at 50% conversion. The *ee* of *anti*-**2** was 69%, *syn*-**2** was 85% and (+)-**1** was 21%. The k_{rel} of this resolution was 1.9 at 50% conversion.

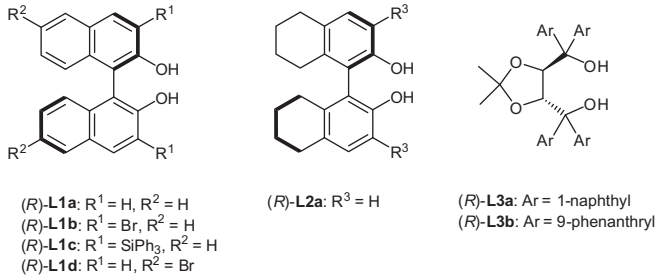


Figure 1. Chiral ligands.

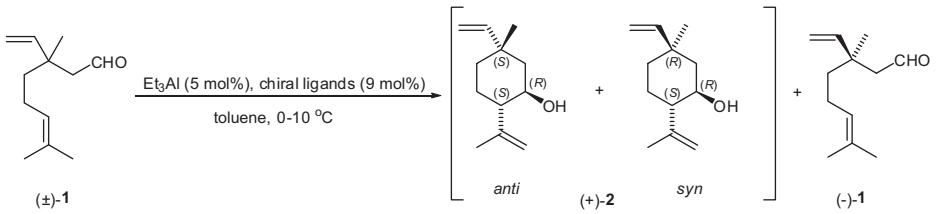
Catalysts with substituted BINOL type ligands led to kinetic resolutions with lower performances than (*R*)-**L1a**-Al and (*S*)-**L1a**-Al. The catalysts with 3,3-substituted BINOLs provided **2** with slower reaction speeds. The reaction with (*R*)-**L1b** reached 37% conversion in 5 h (entry 3). The ratio of *anti*-**2**/*syn*-**2** was 69/31. The *ee* of *anti*-**2** and *syn*-**2** were significantly lower than the reactions with (*R*)-**L1a**, 31% and 26%, respectively. Compound (−)-**1** was obtained with 8% *ee*. The k_{rel} was 1.4 at 46% conversion. The catalyst ((*R*)-**L1c**)-Al seldom afforded **2** in 19 h despite a loading of 10 mol % of the catalyst (entry 4). The 6,6′-substituted BINOL (*R*)-**L1d** also provided **2** with low enantioselectivity at 39% conversion (entry 5).

(*R*)-H8-BINOL (*R*)-**L2a**, with modified aromatic rings, was also used for this resolution. Catalyst (*R*)-**L1d** provided **2** with low enantioselectivity at 48% conversion (entry 6). The ratio of *anti*-2 was 71%. This was slightly higher than the reaction with **L1a**-Al.

The kinetic resolution of (±)-**1** was also carried out using catalysts bearing TADDOL type ligands. The results indicated that (*R*, *R*)-1-naphthyl-TADDOL (*R*)-**L3a**-Al showed a chiral recognition towards (±)-**1** (entries 7 and 8). However, the resolution ability was lower than that obtained with BINOL-Al. The catalyst with one equivalent[19] of (*R*)-**L3a** afforded (+)-**2** with 34% *ee* of *anti*-**2** and 35% *ee* of *syn*-**2**, and an opposite specific rotation of the reaction with (*R*)-BINOL ((*R*)-**L1a**) (entry 7). The ratio of *anti*-**2**/*syn*-**2** was 68%/32% at 27% conversion. The k_{rel} value was 1.1. Catalysts with (*S*)-**L3a** ligands showed almost the same performance except for the specific rotations as well as BINOL (entries 7 and 8). The catalyst bearing (*R*,*R*)-9-phenanthryl-TADDOL (*R*)-**L3b**-Al[20] loaded 10 mol % provided (+)-**2**. The ratio of *anti*-**2** was 72% at 41% conversion when (*R*)-**L3a** was used. The *ee* of *anti*-**2** and *syn*-**2** were 39% and 44%. The diastereoselectivity of *anti*-**2** and enantioselectivity of (+)-**2** were higher than when (*R*)-**L3a** was used.

The results of the kinetic resolution of 3-vinylcitronellal (±)-**1** with (*S*)-BINOL((*S*)-**L1a**)-Al are shown in Table 2. The *ee* of *anti*-**2** gradually decreased as the reaction progressed. The *ee* of *anti*-**2** was 68% at 8% conversion (entry 1, Table 2). The *ee* of *anti*-**2** was slightly then lower than 70% until 50% conversion (entries 2 and 3), and gradually decreased to 60%ee from 50% to 81% conversion (entries 4 and 5). The *ee* value of *syn*-**2** gradually increased over

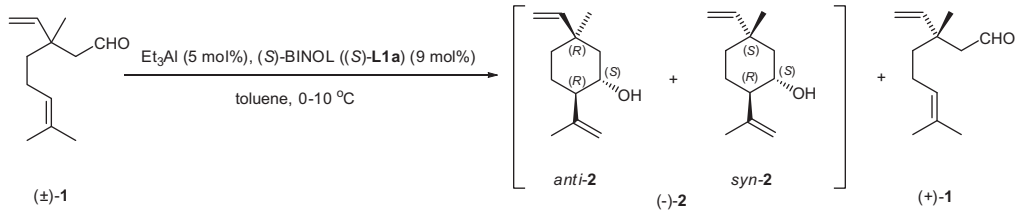
Table 1
Kinetic resolution of racemic 3-vinylcitronellal ((±)-**1**) with aluminum complex with a variety of chiral ligands



Entry	Ligand	Time (h)	Conv.[a] (%)	Ratio of *anti*/*syn*-**2**[a]	*ee* of *anti*/*syn*-**2**[a,b] (%)	*ee* of **1**[a] (%)	k_{rel}[c]
1	(*R*)-**L1a**	0.5	46	68/32	71/89	25	2.3
2	(*S*)-**L1a**	0.5	50	68/32	−69/−85	−21	1.9
3	(*R*)-**L1b**	5	37	69/31	−31/−26	−8	1.4
4[d]	(*R*)-**L1c**	19	3	—	—	<±1	—
5	(*R*)-**L1d**	7	39	67/33	−28/−30	−3	1.1
6[d]	(*R*)-**L2a**	2.5	48	71/29	18/29	−7	1.2
7[e,f]	(*R*)-**L3a**	4	27	66/34	34/35	2	1.1
8[f]	(*S*)-**L3a**	1.5	49	68/32	−31/−34	−6	1.2
9[d,f]	(*R*)-**L3b**	1	41	72/28	39/44	−4	1.2

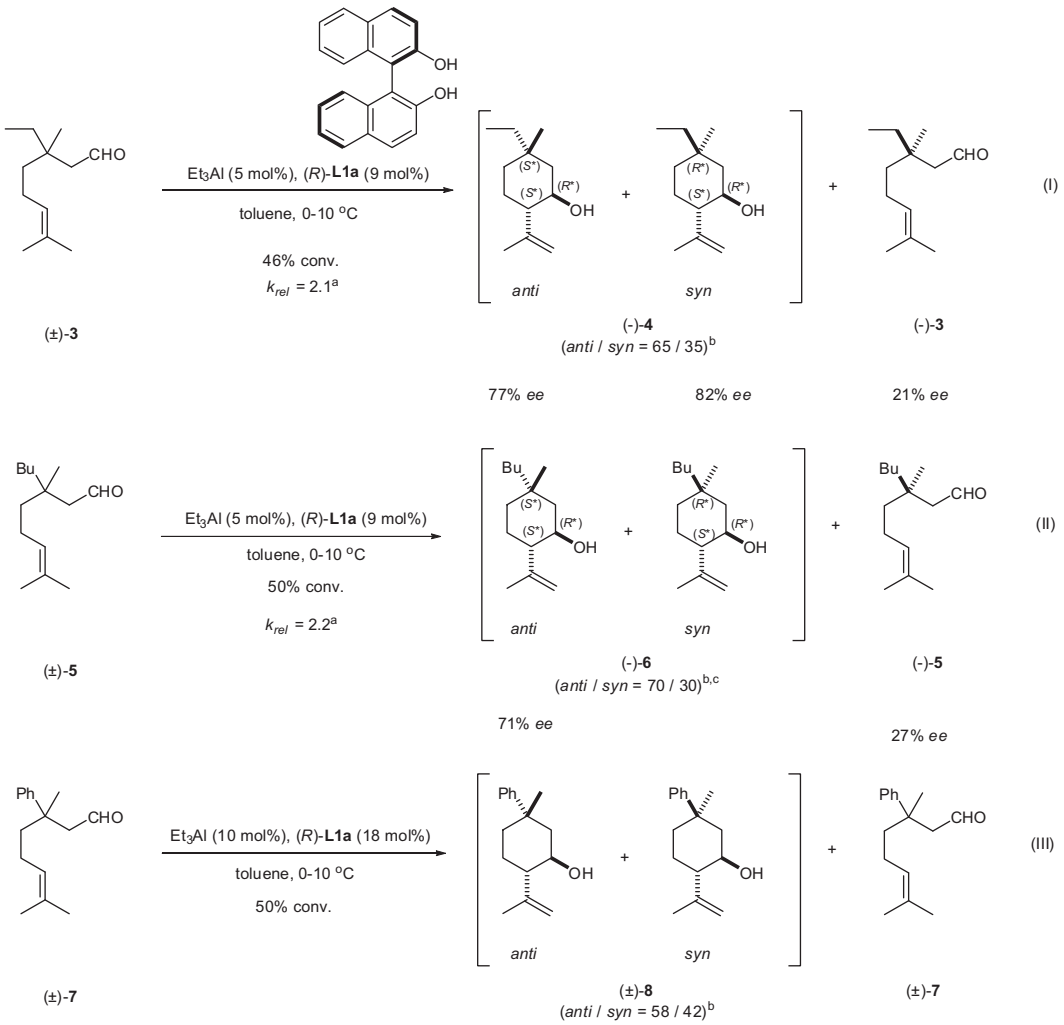
[a] Determined by GC analysis.
[b] Specific rotation was analyzed as a mixture of *anti*-**2** and *syn*-**2**.
[c] Calculated from the first-order rate law using the theoretical conversion value.[18]
[d] 10 mol % of Et_3Al and 18 mol % of ligand were used.
[e] 4 mol % of Et_3Al and 7.2 mol % of (*R*)-**L3a** were used.
[f] Et_3Al:ligand = 1:1.

Table 2
Kinetic resolution of racemic 3-vinylcitronellal (±)-**1** by (*S*)-BINOL ((*S*)-**L1a**)-Al catalyst



Entry	Time (min)	Conv.[a] (%)	Ratio of *anti*-**2**/*syn*-**2**[a]	*ee* of *anti*-**2**[a,b] (%)	*ee* of *syn*-**2**[a,b] (%)	*ee* of **1**[a] (%)	k_{rel}[c]
1	0	8	68/32	68	70	2	1.3
2	15	34	69/31	69	86	12	1.8
3	30	50	68/32	69	85	21	1.9
4	60	69	68/32	62	88	29	1.7
5	90	81	66/34	60	91	30	1.4

[a] Determined by GC analysis.
[b] Specific rotation was analyzed as a mixture of *anti*-**2** and *syn*-**2**.
[c] Calculated from the first-order rate law using the theoretical conversion value.[18]



Scheme 2. Kinetic resolutions of a variety of racemic citronellal analogs with (*R*)-BINOL((*R*)-**L1a**)-Al. [a]Calculated from the first-order rate law using the theoretical conversion value.[18] [b]Specific rotation was analyzed as a mixture of diastereoisomers. [c]We could not find the analysis conditions for *syn*-**6** chirality.

80% from 34% to 81% conversion (entries 2–5). The *ee* of *syn*-**2** reached 91% *ee* at 81% conversion (entry 5). The results of *ee* of the product *anti*-**2** and *syn*-**2** were higher than the product in the kinetic resolution of citronellal.[14] Additionally, the *ee* of **2** was still

maintained over 60% after the conversion reached 50%. The diastereoselectivity of *anti*-**2** was maintained at approximately 68% over the resolution.

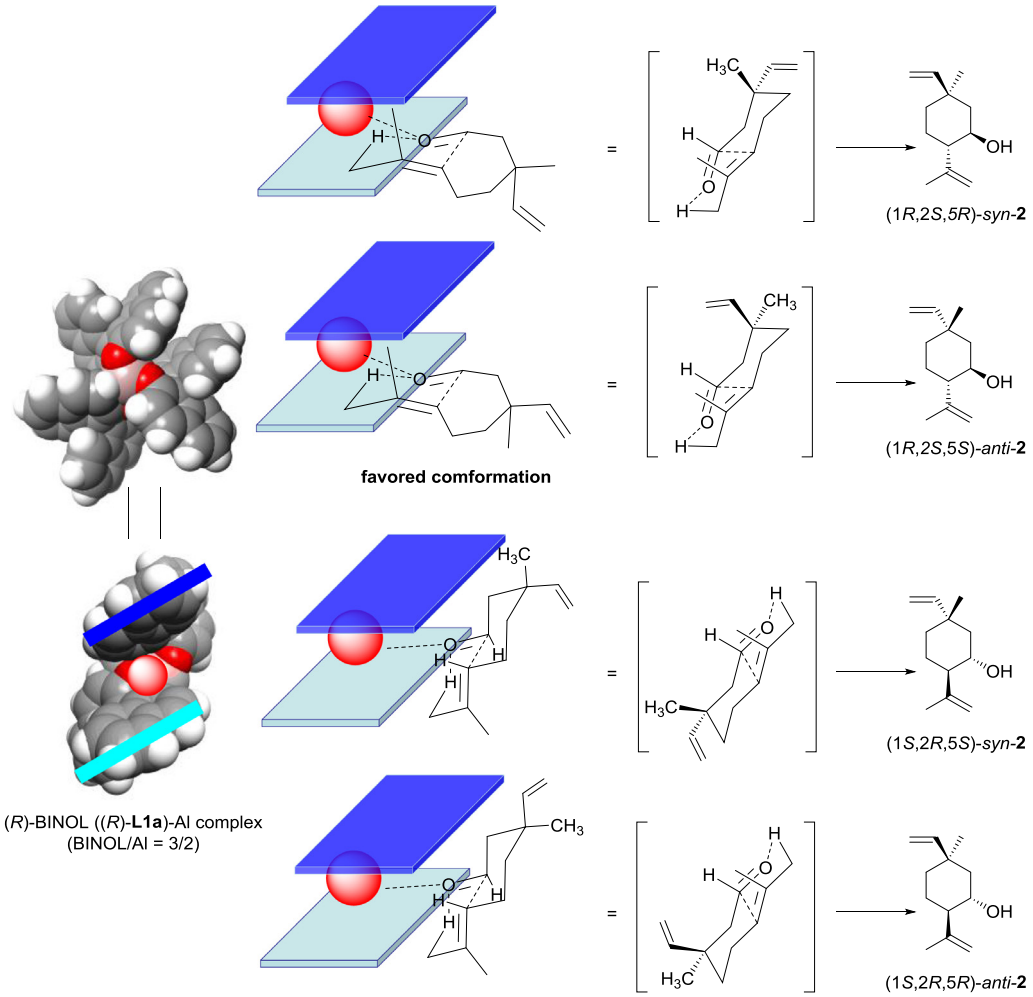
By contrast, the unreacted citronellal analogue (+)-**1** was obtained with low enantioselectivity. The *ee* value of (+)-**1** was 12% at 34% conversion (entry 2). The *ee* of (+)-**1** increased during the resolution. The *ee* of (+)-**1** reached 29% at 50% conversion while the *ee* of *anti*-**2** was 69% and *syn*-**2** was 69% (entry 3). At the start of the reaction, the first-order k_{rel} value[17] calculated with the *ee* of (+)-**1** was only 1.3 (entry 1). As the reaction proceeded, the k_{rel} value was below 2 despite the *ee* values of the products *anti*-**2** and *syn*-**2** being over 60% and 80% respectively (entries 2–5).

The kinetic resolutions of racemic citronellal analogues, 3-ethylcitronellal (±)-**3**,[21,22] 3-butylcitronellal (±)-**5**[21,23] and 3-phenylcitronellal (±)-**7**[21,24] were successfully carried out. The results are shown in Scheme 2. The substrates (±)-**3** and (±)-**5** were highly-reactive compounds and gave the cyclization products by GC injection. These kinetic resolution conversion values were corrected by calculations.

The kinetic resolution of racemic 3-ethylcitronellal (±)-**3** with (*R*)-BINOL((*R*)-**L1a**)-Al gave optically active compounds (−)-**3** and (−)-**4**. The diastereoisomers of **4** were also mainly *anti*-**4** (1α,2β,5β-**4**) and *syn*-**4** (1α,2β,5α-**4**). Other possible isomers were barely detected by GC as well as **2**. The products of the two diastereoisomers, *anti*-**4** and *syn*-**4**, were provided as the opposite stereoisomers by the confirmation from the chiral-GC chart of the remaining (−)-**3** cyclized by Al-MCM41 to **4**.[25] It showed that the major stereoisomer of *anti*-**4** was opposite to that of the major stereoisomer peak of *anti*-**4** cyclized by (*R*)-BINOL ((*R*)-**L1a**)-Al in the same way as the resolution of (±)-**1**. (−)-5-Ethylisopulegol (−)-**4** was obtained in this resolution. The diastereoselectivity of *anti*-**4** was 65%, which was slightly lower than that of *anti*-**2** at 46% conversion ((I) vs entries 1 and 2, Table 1). The *ee* of *anti*-**4** was 77%, *syn*-**4** was 82% and (−)-**3** was 21%. The k_{rel} was 2.2 at 46% conversion.

Next, in the kinetic resolution of racemic 3-butylcitronellal (±)-**5** with (*R*)-**L1a**-Al, optically active 5-butylisopulegol (−)-**6** was obtained with 70% diastereoselectivity of *anti*-**6** (II). The diastereoisomer of *anti*-**6** was *syn*-**6**. Other isomers were detected as less than 1% by GC as well as the resolution of **2** and **4**. The product *anti*-**6** was obtained with 71% *ee* and (−)-**5** was obtained with 27% *ee* at 50% conversion. The k_{rel} was 2.2 at 50% conversion.

The kinetic resolution of 3-phenylcitronellal (±)-**7** gave racemic products (±)-**8** at 61% conversion (III). 3-Phenylcitronellal (±)-**7** provided (±)-**8** with 58% diastereoselectivity of *anti*-**8** and 42% of *syn*-**8**. The bulky substituent decreases the diastereoselectivity of *anti*-**8** due to the bigger interactions between the catalysts. Thus 3-phenylcitronellal (±)-**7**, which has the biggest substitution of the three analogues, provided **8** with not only the lowest diastereoselectivity but no enantioselectivity of **8** in the kinetic resolution. Thus, it can be seen that the larger substituents at the 3-position of citronellal lead to a lower yield of diastereoselective products and a different tendency of the kinetic resolution.



Scheme 3. Chiral recognition of (*R*)-BINOL((*R*)-**L1a**)-Al catalyst.

3,5-Dimethylheptenal was expected to form the 5-membered ring product. However, trace amounts of the cyclized alcohol were detected in the reaction mixture using GC–MS. Methylcitronellylketone[26] and citronellic acid methyl ester gave no product.

The reaction follows an intramolecular ene reaction mechanism catalysed by an aluminum complex as a Lewis acid.[4,27] The carbonyl group of 3-alkylcitronellal is coordinated to an aluminum active site, then a concerted reaction occurs to create the 6-membered ring, affording 5-alkylisopulegol.

Proposed intermediate states for the reaction are shown in Scheme 3. 3-Vinylcitronellal (±)-**1** was used as a typical substrate for these resolutions. The chiral recognition in these catalysts is a function of the BINOL type ligands **L1** and **L2** or TADDOL type ligands **L3**. These complexes have a metal center between two parallel aromatic rings.[14,28] During the transition state of the ring-closing ene reaction, the aromatic rings are in close proximity to 3-vinylcitronellal. This narrow space results in the good diastereo- and enantioselectivity seen in the reaction.

It is assumed that these aromatic rings are horizontally aligned with respect to each other, so that the edge of the aromatic rings can interact with the 3-vinyl group of (±)-**1** when the carbonyl group coordinates to the aluminium reaction site. 3-Vinylcitronellal (±)-**1** can be fitted between the two parallel aromatic rings of (*R*)-**L1a**-Al when the carbon with the 3-vinyl group is located on the opposite side of the aluminium reaction site. The bulky 3-vinyl and 3-methyl substituents form the transition state into a *cis*-decalin type conformation when the carbonyl group of (±)-**1** approaches the aluminium reaction site. In addition, the propan-2-ylidene group in **1** can fit into the outside edge of the narrow space of the aromatic rings. Therefore these interactions between the aromatic rings and **1** result in the formation of *anti*-**2** and *syn*-**2** with high enantioselectivity (I and II). The narrow spacing of the aromatic rings prohibits **1** from forming the other isomers of **2**.[27]

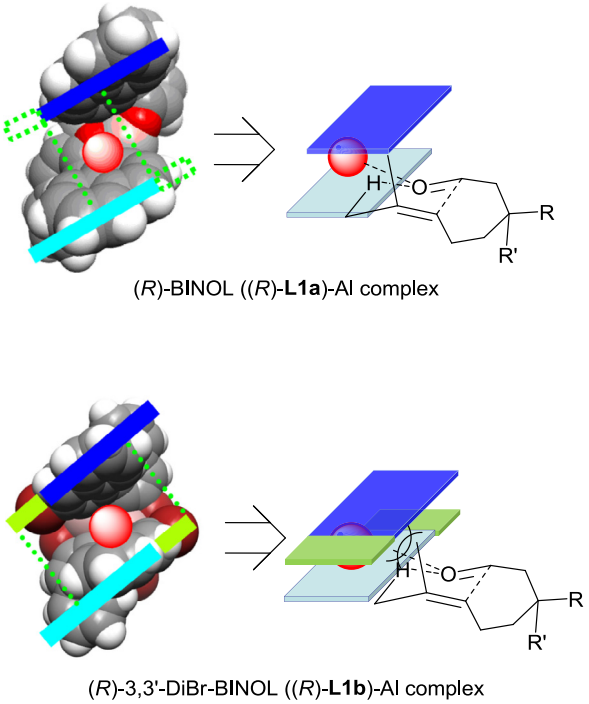


Figure 2. Chiral recognition of (*R*)-BINOL((*R*)-**L1a**)-Al and (*R*)-3,3′-diBr-BINOL((*R*)-**L1b**)-Al catalysts.

When BINOL is substituted with bromine **L1b** or triphenylsilyl groups **L1c**, the BINOL ring expand horizontally and become more spatially similar, thus affording less chiral recognition (Fig. 2). (*R*)-H8-BINOL **L2a** gives more bulky ring edges on its catalyst. The 3-vinyl and methyl groups of **2** do not fit into the reaction site by the bulky obstacle and afford far lower selectivity and enantioselectivity of **2**.[13,28] 1-NaphTADDOL(**L3a**)-Al also bears the same type of aromatic rings, consisting of 1-naphthyl groups. These rings are more flexible than those in BINOL-Al and thus afford **2** with lower enantioselectivity. 9-PhenanthrylTADDOL (**L3b**)-Al has more bulky aromatic rings than **L3a**-Al. The aromatic rings of **L3b** prevent (±)-**1** from approaching to aluminum active site. Therefore **L3b**-Al showed milder reactivity than **L3a**-Al.

3-Ethylcitronellal **3** and 3-butylcitronellal **5** followed the manner of chiral recognition of these aluminium catalysts. However, 3-phenylcitronellal **7** has a more bulky substituent at its 3-carbon group. The phenyl group is an obstacle the cyclization when the carbonyl group of 3-phenylcitronellal approaches the gap between the aromatic rings, the near point of the aluminium reaction site. Hence the chiral recognition does not function and **7** gives racemic **8**.

The scents of the isopulegol analogues were evaluated. Analogues (−)-**2**, (−)-**4**, (−)-**6** and (±)-**8** have a floral green note. As an additional characteristic, 5-ethylisopulegol (−)-**4** has a fruity note. (−)-5-Butyl isopulegol (−)-**6** has a similar scent to (−)-**2** with a tobacco facet. Racemic 5-phenylisopulegol (±)-**1** has a rose note and some strong cinnamon aspect.

3. Conclusion

The chiral aluminum catalyst (*R*)-BINOL-Al performed kinetic resolution of citronellal analogues. Racemic 3-alkylcitronellal gave optically active 5-alkylisopulegol respectively with high enantioselectivity. Unreacted citronellal analogues were obtained with low enantioselectivity. The two main diastereoisomers of the products were opposite stereoisomers to each other. The larger substituents at the 3-position of citronellal afforded diastereoselective products in lower yields and a different tendency of the kinetic resolution from that of citronellal. All of the isopulegol analogues have a floral green note.

4. Experimental

4.1. General

Gas liquid chromatography (GC) was performed with a GC-2010AF system (Shimadzu) or GC-353B (GL science) and D-2500 (Hitachi) using DB-WAX (30 m × 0.32 mm × 0.5 μm), IC-1 (30 m × 0.25 mm × 0.25 μm), Chirasil-DEX-CB (25 m × 0.25 mm × 0.25 μm), Beta DEX™ 225 (30 m × 0.25 mm × 0.25 μm), and Beta DEX™ 325 (30 m × 0.25 mm × 0.25 μm) columns. Gas chromatography–mass spectrometry (GC–MS) was performed with a GC-QP2010 system (Shimadzu) using Rtx-1 (30 m × 0.25 mm × 0.25 μm) columns. ^{1}H NMR spectra were recorded on a Varian 500 Hz spectrometer. Chloroform was used as NMR solvent and chemical shifts are reported as δ values in parts per million relative to trimethysilane ($\delta = 0$). Optical rotations were determined on a JASCO P-1020 digital polarimeter (JASCO). Molecular orbital calculation was preceded by SCIGRESS V2 powered by Fujitsu. Graphical drawings were performed with a Mathematica program. All other reagents were purchased from Sigma–Aldrich, Wako Pure Chemical Industries, Ltd, Nacalai Tesque, Inc., Takasago International Corporation, or Strem Chemicals Inc. They were used as-received. All compounds used were of commercial grade.

4.2. General procedure of citronellal analogues (±)-1, (±)-3, (±)-5 and (±)-7 kinetic resolution by a ring-closing ene reaction catalyzed by (*R*)-BINOL-Al

A mixture of (*R*)-BINOL (*R*)-**L1a** (57.2 mg, 0.200 mmol, 5 mol %, 1.8 equiv vs Al), triethylaluminium 1.0 mol/L toluene solution (0.11 mL, 0.110 mmol, 5 mol %), and toluene (1.2 mL) as added to a 50-mL Schlenk tube under an N_2 atmosphere. After being stirred at rt for over 1 h, the solution was cooled to less than 10 °C. The citronellal analogue (2.22 mmol) was added dropwise slowly under 10 °C and stirred for a given amount of time. Samples of the solution were consecutively taken at given time periods and analyzed by GC. The citronellal analogues in the reaction mixture were collected by silica-gel column chromatography or preparative TLC separation (heptane/AcOEt = 7/1) with 2,6-diphenylphenol and reacted by Al-MCM-41 (cat. amount) in toluene at 80 °C in order to analyze their enantioselectivity.[23] The authentic samples of racemic **2**, **4**, **6** and **8** were also prepared by cyclization catalyzed by Al-MCM-41.

4.3. (*R*)-(−)-3-Vinyl-3,7-dimethyloct-6-enal ((*R*)-(−)-3-vinylcitronellal) (−)-1 (Table 1, entry 1)

Obtained as a yellowish oil. Yield 152 mg from 400 mg of (±)-**1** (38%). $[\alpha]_D^{20}$ = −14.1 (*c* 0.08, EtOH, 25% *ee*); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.16 (3H, s), 1.39–1.47 (2H, m), 1.58 (3H, s), 1.67 (3H, s), 1.92 (2H, q, *J* 8.3 Hz), 2.34 (2H, qd, *J* 14.9, 2.8 Hz), 5.02 (1H, d, *J* 17.6 Hz), 5.03–5.9 (1H, m), 5.11(1H, d, *J* 10.8 Hz), 5.85 (1H, dd, *J* 17.6, 10.9 Hz), 9.73 (1H, t, 2.8 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): 17.6 (CH_3), 22.6 (CH_2), 23.4 (CH_3), 25.6 (CH_3), 39.0 (C), 41.4 (CH_2), 53.1 (CH_2), 113.2 (CH_2), 124.0 (CH), 131.8 (C), 145.0 (CH), 203.3 (CHO); HRMS (FI): M^+, found 180.1502. $C_{12}H_{20}O$ requires 180.1514.

4.4. (+)-5-Vinyl-5-methyl-2-(prop-1-en-2-yl)cyclohexanol ((+)-5-vinylisopulegol) (+)-2 (1*R*,2*S*,5*S*/1*R*,2*S*,5*R* = 68/32) (absolute stereochemistry) (Table 1, entry 1)

Obtained as a colorless oil. Yield 189 mg from 400 mg of (±)-**1** (47%). $[\alpha]_D^{20}$ = +9.7 (*c* 0.11, EtOH, 71% *ee* (*anti*-**2**), 89%*ee* (*syn*-**2**)); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.01 (3H, s), 1.20–1.34 (3H, m), 1.42–1.65 (4H, m), 1.69 (3H, s), 1.70–1.80 (1H, m), 1.87–1.92 (1H, m), 2.10 (1H, ddd, *J* 12.9, 3.7, 2.6 Hz), 4.84–5.07 (3H, m), 5.75 (1H, dd, *J* 17.7, 11.0 Hz) (major); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.05 (3H, s), 1.20–1.65 (8H, m), 1.75 (3H, s), 1.82–1.92 (2H, m), 4.84–5.07 (3H, m), 5.82 (1H, dd, *J* 17.5, 1.8 Hz) (minor); ^{13}C NMR (125 MHz, $CDCl_3$): 19.2 (CH_3), 26.4 (CH), 31.5 (CH_3), 36.9 (CH_2), 38.9 (C), 44.8 (CH_2), 54.7 (CH), 67.3 (CH), 112.4 (CH_2), 112.9 (CH_2), 145.9 (CH), 146.6 (C) (major); ^{13}C NMR (125 MHz, $CDCl_3$): 19.3 (CH_3), 22.7 (CH_3), 25.9 (CH_2), 36.1 (CH_2), 37.8 (C), 43.9 (CH_2), 54.7 (CH), 67.4 (CH), 109.4 (CH_2), 112.9 (CH_2), 146.4 (C), 149.9 (CH) (minor); HRMS (FI): M^+, found 182.1676. $C_{12}H_{20}O$ requires 182.1671 (mixture).

4.5. (*S*)-(5-Methyl-2-(prop-1-en-2-yl)-5-vinylcyclohexyl)3,3,3-trifluoro-2-methoxy-2-phenylpropanoate (1*R*,2*S*,5*S*/1*R*,2*S*,5*R* = 68/32) ((*S*)-MTPA ester of (+)-2)[17]

^{1}H NMR (500 MHz, $CDCl_3$): δ 1.00 (3H, s), 1.21–1.60 (4H, m), 1.66 (3H, t, *J* 0.9 Hz), 2.12–2.22 (3H, m), 3.52 (3H, d, *J* 1.1 Hz), 4.77–4.86 (3H, m), 4.92 (1H, dd, *J* 15.7, 1.0 Hz), 5.16 (1H, dd, *J* 10.9, 0.9 Hz), 5.18–5.27 (1H, m), 7.35–7.60 (5H, m) (major); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.16 (3H, s), 1.21–1.71 (4H, m), 1.73 (3H, t, *J* 0.9 Hz), 1.81–1.87 (1H, m), 2.15–2.28 (2H, m), 3.56 (3H, d, *J* 1.3 Hz), 4.77–4.86 (3H, m), 4.90 (1H, dd, *J* 8.0, 1.0 Hz), 5.25 (1H, dd, *J* 17.8, 0.8 Hz), 5.27–5.34 (1H, m), 7.35–7.60 (5H, m) (minor); ^{13}C NMR (125 MHz, $CDCl_3$): 19.9 (CH_3), 27.8 (CH_2), 31.3 (CH_3), 37.1 (CH_2), 38.8 (C), 40.6 (CH_2), 50.2 (CH), 55.9 (CH_3), 74.9 (CH), 84.8 (C), 112.2 (CH_2), 113.5 (CH_2), 121.5 (C), 123.8 (C), 126.1 (C), 127.5 (CH), 128.2 (CH), 128.7 (CH), 129.4 (CH), 129.7 (CH), 144.8 (CH), 146.1 (C) (major); ^{13}C NMR (125 MHz, $CDCl_3$): 22.2 (CH_3), 27.1 (CH_2), 31.3 (CH_3), 35.8 (CH_2), 37.8 (C), 41.1 (CH_2), 50.5 (CH), 55.4 (CH_3), 74.7 (CH), 85.0 (C), 112.5 (CH_2), 113.5 (CH_2), 121.5 (C), 123.8 (C), 127.5 (C), 127.5 (CH), 128.2 (CH), 128.7 (CH), 129.4 (CH), 129.7 (CH), 145.9 (C), 148.9 (CH) (minor).

4.6. (*R*)-(5-Methyl-2-(prop-1-en-2-yl)-5-vinylcyclohexyl)3,3,3-trifluoro-2-methoxy-2-phenylpropanoate (1*R*,2*S*,5*S*/1*R*,2*S*,5*R* = 68/32) ((*R*)-MTPA ester of (+)-2)[17]

^{1}H NMR (500 MHz, $CDCl_3$): δ 1.03 (3H, s), 1.23–1.51 (3H, m), 1.53 (3H, br), 1.55–1.72 (2H, m), 2.10–2.14 (1H, m), 2.19–2.24 (1H, m), 3.57 (3H, s), 4.58–4.84 (3H, m), 4.96 (1H, dd, *J* 17.5, 1.0 Hz), 5.16 (1H, dd, *J* 10.9, 0.8 Hz), 5.18–5.27 (1H, m), 7.35–7.60 (5H, m) (major); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.14 (3H, s), 1.21–1.71 (4H, m), 1.60 (3H, br), 1.87–1.93 (1H, m), 2.19–2.27 (2H, m), 3.52 (3H, s), 4.77–4.86 (3H, m), 4.91 (1H, dd, *J* 10.7, 1.0 Hz), 5.22–53.4 (2H, m), 7.35–7.60 (5H, m) (minor); ^{13}C NMR (125 MHz, $CDCl_3$): 19.9 (CH_3), 27.3 (CH_2), 30.5 (CH_3), 37.1 (CH_2), 38.4 (C), 40.6 (CH_2), 50.2 (CH), 55.9 (CH_3), 74.9 (CH), 84.8 (C), 112.2 (CH_2), 113.5 (CH_2), 121.5 (C), 123.8 (C), 126.1 (C), 127.5 (CH), 128.2 (CH), 128.7 (CH), 129.4 (CH), 129.7 (CH), 144.8 (CH), 146.1 (C) (major); ^{13}C NMR (125 MHz, $CDCl_3$): 22.2 (CH_3), 27.3 (CH_2), 30.5 (CH_3), 35.8 (CH_2), 37.3 (C), 41.1 (CH_2), 50.5 (CH), 55.4 (CH_3), 74.7 (CH), 85.0 (C), 112.5 (CH_2), 113.5 (CH_2), 121.5 (C), 123.8 (C), 127.5 (C), 127.5 (CH), 128.2 (CH), 128.7 (CH), 129.4 (CH), 129.7 (CH), 145.9 (C), 148.9 (CH) (minor).

4.7. (*S*)-(+)-3-Vinyl-3,7-dimethyloct-6-enal ((*S*)-(+)-3-vinylcitronellal) (+)-1 (Table 1, entry 2)

Obtained as a yellow oil. Yield 48 mg at 81% conversion from 400 mg of (±)-**1** (12%). $[\alpha]_D^{20}$ = +11.6 (*c* 0.08, EtOH, 30% *ee*); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.15 (3H, s), 1.39–1.45 (2H, m), 1.57 (3H, s), 1.67 (3H, s), 1.89–1.94 (2H, m), 2.29–2.40 (2H, m), 5.00 (1H, d, *J* 17.6 Hz), 5.03–5.9 (1H, m), 5.12(1H, d, *J* 10.8 Hz), 5.82 (1H, dd, *J* 17.5, 10.9 Hz), 9.72 (1H, t, 2.8 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): 17.5 (CH_3), 22.5 (CH_2), 23.4 (CH_3), 25.6 (CH_3), 38.9 (C), 41.3 (CH_2), 53.0 (CH_2), 113.1 (CH_2), 124.0 (CH), 131.7 (C), 145.0 (CH), 203.2 (CHO); HRMS (FI): M^+, found 180.1513. $C_{12}H_{20}O$ requires 180.1514.

4.8. (−)-5-Vinyl-5-methyl-2-(prop-1-en-2-yl)cyclohexanol ((−)-5-vinylisopulegol) (−)-2 (1*S*,2*R*,5*R*/1*S*,2*R*,5*S* = 66/34) (absolute stereochemistry) (Table 1, entry 2)

Obtained as a colorless oil. Yield 195 mg at 81% conversion from 400 mg of (±)-**1** (49%). $[\alpha]_D^{20}$ = −8.8 (*c* 0.03, EtOH, 60% *ee* (*anti*-**2**), 91%*ee* (*syn*-**2**)); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.02 (3H, s), 1.20–1.34 (3H, m), 1.42–1.65 (4H, m), 1.69 (3H, s), 1.70–1.80 (1H, m), 1.87–1.92 (1H, m), 2.10 (1H, ddd, *J* 12.9, 3.7, 2.6 Hz), 4.83–5.08 (3H, m), 5.75 (1H, dd, *J* 17.7, 11.1 Hz) (major); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.05 (3H, s), 1.20–1.65 (8H, m), 1.75 (3H, s), 1.82–1.92 (2H, m), 4.83–5.08 (3H, m), 5.82 (1H, dd, *J* 17.5, 1.8 Hz) (minor); ^{13}C NMR (125 MHz, $CDCl_3$): 19.2 (CH_3), 26.4 (CH), 31.5 (CH_3), 36.9 (CH_2), 38.9 (C), 44.8 (CH_2), 54.7 (CH), 67.3 (CH), 112.5 (CH_2), 112.9 (CH_2), 145.9 (CH), 146.6 (C) (major); ^{13}C NMR (125 MHz, $CDCl_3$): 19.3 (CH_3), 22.7 (CH_3), 25.9 (CH_2), 36.1 (CH_2), 37.8 (C), 43.9 (CH_2), 54.7 (CH), 67.4 (CH), 109.4 (CH_2), 112.9 (CH_2), 146.4 (C), 149.9 (CH) (minor); HRMS (FI): M^+, found 182.1676. $C_{12}H_{20}O$ requires 180.1514 (mixture).

4.9. (−)-3-Ethyl-3,7-dimethyloct-6-enal ((−)-3-ethylcitronellal) ((−)-3) (Scheme 2, I)

Obtained as a yellowish oil. Yield 125 mg at 57% conversion from 700 mg of (±)-**3** (18%). $[\alpha]_D^{20} = -1.1$ (*c* 0.01, $CHCl_3$, 32% *ee*); ^1H NMR (500 MHz, $CDCl_3$): δ 0.86 (3H, t, *J* 7.5 Hz), 1.03 (3H, s), 1.28–1.47 (4H, m), 1.60 (3H, s), 1.68 (3H, br), 1.90–1.98 (2H, m), 2.27 (2H, d, *J* 3.2 Hz), 5.00–5.15 (1H, m), 9.84 (1H, t, *J* 3.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): 8.0 (CH_3), 17.6 (CH_3), 22.3 (CH_3), 24.8 (CH_3), 25.6 (CH_3), 32.3 (CH_2), 36.2 (C), 39.6 (CH_2), 52.4 (CH_2), 124.3 (CH), 131.6 (C), 203.8 (CHO); HRMS (FI): M^+, found 182.1653. $C_{12}H_{22}O$ requires 182.1671.

4.10. (−)-5-Ethyl-5-methyl-2-(prop-1-en-2-yl)cyclohexanol ((−)-3-ethylisopulegol) (−)-4 (1*R**,2*S**,5*S**/1*R**,2*S**,5*R** = 65/35) (relative stereochemistry) (Scheme 2, I)

Obtained as a colorless oil. Yield 364 mg at 57% conversion from 700 mg of (±)-**3** (52%). $[\alpha]_D^{20} = -7.17$ (*c* 0.24, $CHCl_3$, 73% *ee* (*anti*-**4**), 79% *ee* (*syn*-**4**)); ^1H NMR (500 MHz, $CDCl_3$): δ 0.81–0.87 (3H, m), 0.90 (3H, s), 1.03–1.60 (7H, m), 1.77 (3H, br), 1.78–1.96 (3H, m), 3.66 (1H, ddd, *J* 10.5, 10.5, 4.5 Hz), 4.85–4.92 (2H, m) (major); ^1H NMR (500 MHz, $CDCl_3$): δ 0.82–0.85 (3H, m), 0.87 (3H, s), 1.02–1.60 (7H, m), 1.73 (3H, br), 1.80–1.96 (3H, m), 3.60 (1H, ddd, *J* 10.7, 10.7, 4.5 Hz), 4.85–4.92 (2H, m) (minor); ^{13}C NMR (125 MHz, $CDCl_3$): 7.6 (CH_3), 19.3 (CH_3), 22.1 (CH_3), 26.1 (CH_2), 34.7 (C), 36.4 (CH_2), 38.2 (CH_2), 44.6 (CH_2), 55.1 (CH), 67.6 (CH), 112.7 (CH_2), 146.7 (C) (major); ^{13}C NMR (125 MHz, $CDCl_3$): 7.9 (CH_3), 19.3 (CH_3), 22.1 (CH_3), 25.8 (CH_2), 34.7 (C), 36.6 (CH_2), 38.2 (CH_2), 44.6 (CH_2), 54.8 (CH), 67.1 (CH), 112.7 (CH_2), 146.7 (C) (minor); HRMS (FI): M^+, found 182.1676. $C_{12}H_{22}O$ requires 182.1671 (mixture).

4.11. (−)-3-*n*Butyl-3,7-dimethyloct-6-enal ((−)-3-buthylcitronellal) (−)-5 (Scheme 2, II)

Obtained as a yellowish oil. Yield 878 mg from 2.00 g of (±)-**5** (44%). $[\alpha]_D^{20} = -10.9$ (*c* 0.63, $CHCl_3$, 27% *ee*); ^1H NMR (500 MHz, $CDCl_3$): δ 0.91 (3H, t, *J* 6.9 Hz), 1.04 (3H, s), 1.20–1.38 (8H, m), 1.60 (3H, s), 1.68 (3H, s), 1.90–1.98 (2H, m), 2.27 (2H, d, *J* 3.2 Hz), 5.05–5.11 (1H, m), 9.85 (1H, t, *J* 3.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): 14.2 (CH_3), 17.6 (CH_3), 22.3 (CH_2), 23.6 (CH_2), 25.3 (CH_3), 25.7 (CH_3), 25.8 (CH_2), 36.1 (C), 39.7 (CH_2), 40.1 (CH_2), 52.9 (CH_2), 124.3 (CH), 131.5 (C), 203.9 (CHO); HRMS (FI): M^+, found 210.1969. $C_{14}H_{26}O$ requires 210.1984.

4.12. (−)-5-*n*Butyl-5-methyl-2-(prop-1-en-2-yl)cyclohexanol ((−)-3-buthylisopulegol) ((−)-6) (1*R**,2*S**,5*S**/1*R**,2*S**,5*R** = 70/30) (Scheme 2, II)

Obtained as a colorless oil. Yield 848 mg from 2.00 g of (±)-**5** (42%). $[\alpha]_D^{20} = -76.7$ (*c* 0.60, $CHCl_3$, 71% *ee*, (*anti*-**6**)); ^1H NMR (500 MHz, $CDCl_3$): δ 0.91–1.07 (6H, m), 1.10 (1H, t *J* 11.7 Hz), 1.14–1.41 (7H, m), 1.43–1.62 (3H, m), 1.74 (3H, s), 1.77–1.91 (3H, m), 3.65 (1H, ddd, *J* 10.7, 10.7, 4.4 Hz), 4.88 (2H, d, *J* 20.4 Hz) (major); ^1H NMR (500 MHz, $CDCl_3$): δ 0.88–0.91 (6H, m), 1.05 (1H, t, *J* 11.7 Hz), 1.14–1.41 (7H, m), 1.43–1.62 (3H, m), 1.75 (3H, br), 1.77–1.91 (3H, m), 3.61 (1H, ddd, *J* 10.8, 10.5, 4.2 Hz), 4.88 (2H, d, *J* 20.4 Hz) (minor); ^{13}C NMR (125 MHz, $CDCl_3$): 14.1 (CH_3), 19.3 (CH_3), 22.7 (CH_3), 23.6 (CH_2), 25.4 (CH_2), 26.1 (CH_2), 34.7 (C), 36.9 (CH_2), 45.1 (CH_2), 45.9 (CH_2), 55.1 (CH), 67.6 (CH), 112.7 (CH_2), 146.7 (C) (major); ^{13}C NMR (125 MHz, $CDCl_3$): 14.1 (CH_3), 19.3 (CH_3), 23.5 (CH_2), 25.4 (CH_2), 25.8 (CH_2), 29.4 (CH_3), 34.7 (C), 37.1 (CH_2), 44.9 (CH_2), 45.9 (CH_2), 54.8 (CH), 67.1 (CH), 112.7 (CH_2), 146.7 (C) (minor); HRMS (FI): M^+, found 210.1973. $C_{14}H_{26}O$ requires 210.1984 (mixture).

4.13. 5-Methyl-5-phenyl-2-(prop-1-en-2-yl)cyclohexanol (3-phenylisopulegol) 8 (1α,2β,5β/1α,2β,5α = 58/42) (Scheme 2, III)

Obtained as a colorless oil. Yield 244 mg from 500 mg of (±)-**7** (49%). ^1H NMR (500 MHz, $CDCl_3$): δ 1.20 (3H, s), 1.35–1.50 (2H, m), 1.52 (3H, s), 1.54–1.73 (4H, m), 1.90–2.07 (2H, m), 2.37 (1H, dq, *J* 13.8, 3.0 Hz), 2.71 (1H, dt, *J* 13.4, 3.0 Hz), 3.85 (1H, ddd, *J* 10.5, 10.5, 4.5 Hz), 4.79 (2H, d, *J* 19.9 Hz), 7.10–7.45 (5H, m) (major); ^1H NMR (500 MHz, $CDCl_3$): δ 1.31 (3H, s), 1.35–1.73 (6H, m), 1.77 (3H, s), 1.86–2.07 (3H, m), 2.29 (1H, dq, *J* 12.5, 1.9 Hz), 3.45 (1H, ddd, *J* 10.6, 10.6, 4.7 Hz) 4.92 (2H, d, *J* 18.7 Hz), 7.10–7.45 (5H, m) (minor); ^{13}C NMR (125 MHz, $CDCl_3$): 19.1 (CH_3), 26.4 (CH_2), 35.3 (CH_3), 36.9 (CH_2), 40.0 (C), 44.9 (CH_2), 54.8 (CH), 67.3 (CH), 112.7 (CH), 124.8 (CH), 125.7 (CH), 125.8 (CH), 128.2 (CH), 128.5 (CH), 146.3 (C), 151.2 (C) (major); ^{13}C NMR (125 MHz, $CDCl_3$): 19.3 (CH_3), 25.4 (CH_3), 26.3 (CH_2), 37.0 (CH_2), 38.7 (C), 44.8 (CH_2), 54.5 (CH), 67.8 (CH), 112.9 (CH), 124.8 (CH), 125.5 (CH), 125.8 (CH), 128.2 (CH), 128.5 (CH), 146.6 (C), 151.2 (C) (minor); HRMS (FI): M^+, found 230.1644. $C_{14}H_{26}O$ requires 230.1670 (mixture).

Acknowledgments

We would like to thank Mr. Dean Walker for checking and correcting some errors in English in this manuscript.

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