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Sterically controlled rhenium-catalyzed hydroxyl transposition

Edouard Caron-Duval and Claude Spino*

Université de Sherbrooke, Département de chimie, 2500 Boul. Université, Sherbrooke, QC, J1K 2R1, Canada
Email: Claude.Spino@USherbrooke.ca

We dedicate this work to our dear colleague Samir Zard and congratulate him for a brilliant and inspirational career

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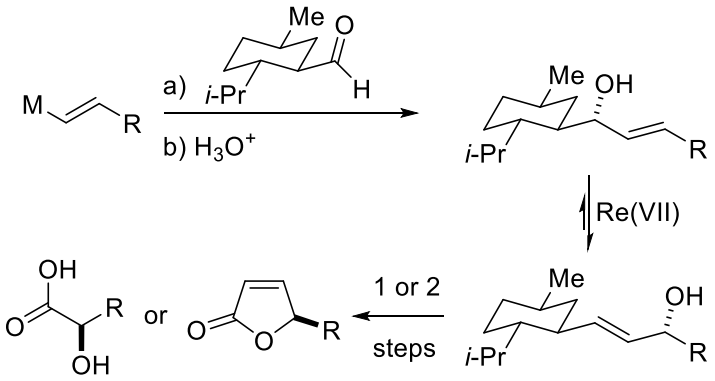
Abstract

Easily prepared vinyliodides are transformed in a few steps into enantiomerically pure alcohol or lactone synthons. The key transformation involves the highly regioselective rhenium(VII)-catalyzed transposition of an allylic alcohol that was prepared by stereoselective addition of a vinyllithium to *p*-menthane-3-carboxaldehyde.

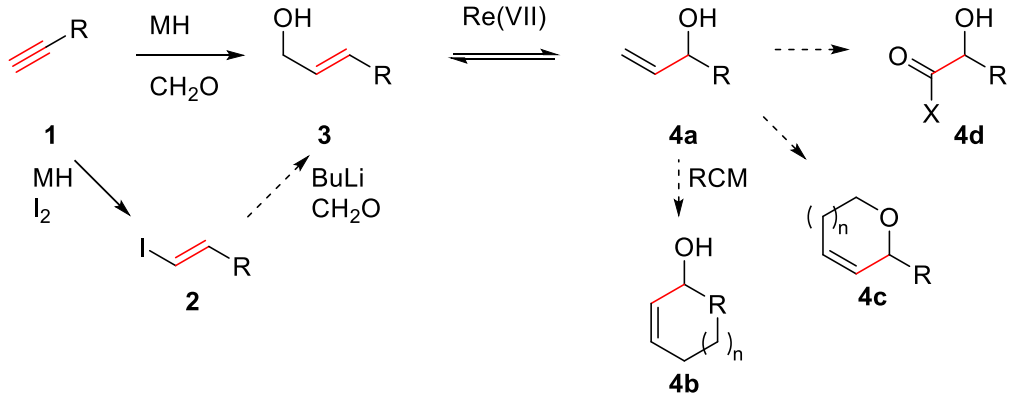


Keywords: *p*-Menthane-3-carboxaldehyde, allylic transposition, Re(VII) catalysis, chiral alcohols, chiral auxiliary.

Introduction

Since the first reports on the high efficiency of trioxorhenium species as catalysts for the isomerization of allylic alcohols,[1-3] chemists have strived to control the position of the equilibrium between the two regioisomeric alcohols **3** and **4** in the hope of favouring a single form (Scheme 1). Among the first strategies conceived was conjugation of the double bond, which procures good stabilization and is rather efficient at biasing the system in favour of the conjugated regioisomer.[4-6] In absence of conjugation, a tertiary allylic alcohol usually predominates over the other regioisomer, but the selectivity is not always pronounced.[4] The ratios of regioisomers obtained when a secondary and a primary alcohol compete is particularly weak.[7] Other strategies include intercepting the primary alcohol with a bulky protecting group,[5] and trapping the hydroxyl group of one isomer with boron,[8] with an epoxyde,[9] or as an acetal.[10-12] In the latter systems, the trapping moieties are part of the structure and are not meant to be removed, limiting the applicability of the method to this type of substrate. Rhenium(VII) has also been used to catalyze the regioselective nucleophilic displacement of allylic alcohols.[13-15] More ways of controlling the position of the equilibrium between allylic alcohols are still needed to increase the scope of this useful catalytic transformation.

Alkynes (**1**) are easy to prepare and, via their hydrometallation, can lead to alcohols **3**, directly or via the corresponding vinylhalide **2** (Scheme 1). In the case where the regioisomer **4** would be needed, the Re(VII)-catalyzed transposition would likely give an unusable mixture of both regioisomers **3** and **4**.[4-7] We now wish to report that the chiral auxiliary *p*-menthane-3-carboxaldehyde may be used to supply a very high regioisomeric ratio of chiral non racemic allylic alcohols upon treatment with 2% Re(VII) catalyst under mild conditions. Cleavage of the chiral auxiliary leads directly to useful synthons and recovery of the auxiliary.

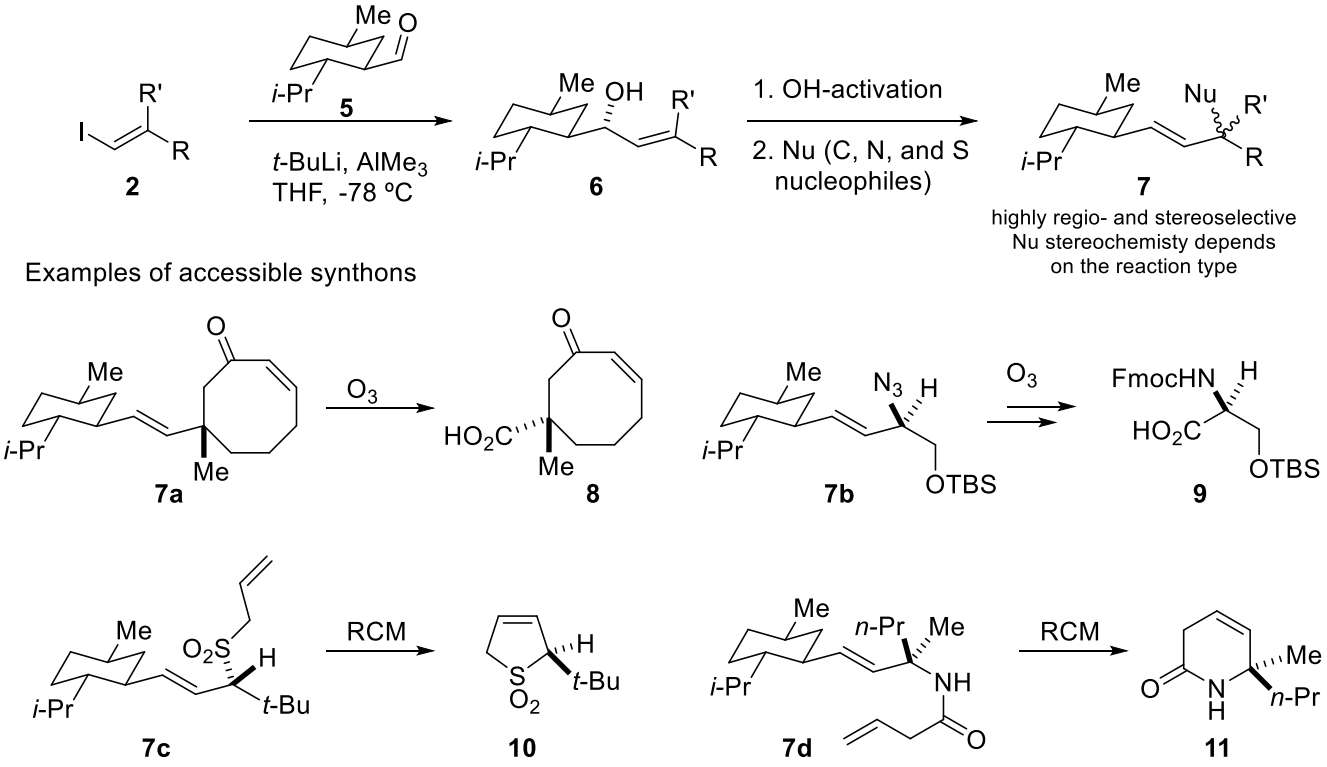


Scheme 1. Alkynes as precursors to allylic alcohols as synthons.

Results and Discussion

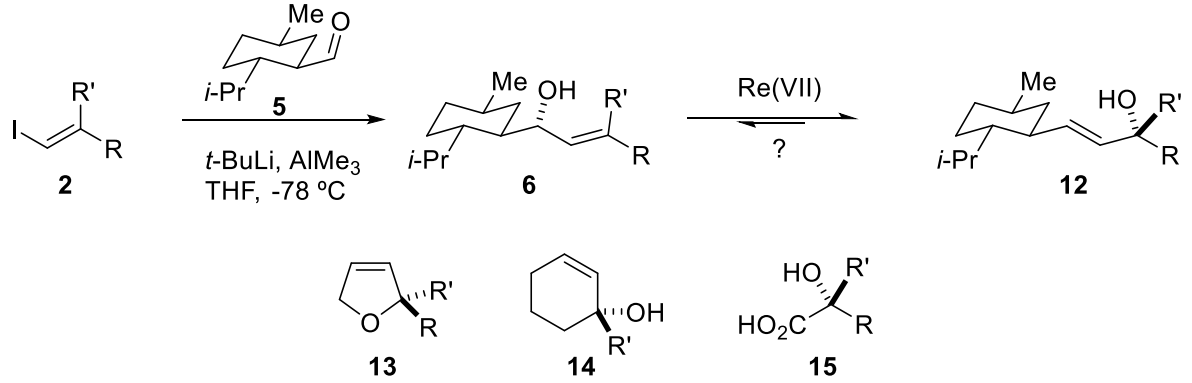
We have developed *p*-methane-3-carboxaldehyde **5** (which we commonly call menthylaldehyde) to access chiral synthons like products **8**-**11** reliably and efficiently (Scheme 2).[16] The alcohols **6** are typically prepared enantiomerically and diastereomerically pure in good yields from alkenylmetals and, after proper activation, the hydroxyl can be regio- and stereoselectively transposed to isomers **7**. We have successfully transposed the hydroxyl group with carbon, nitrogen or sulfur nucleophiles using rearrangements or S_N2' reactions.[16] One of the main attractiveness of the method is that the auxiliary can be cleaved oxidatively to give acids or

aldehydes like **9** or by ring-closing metathesis (RCM) to access such carbo- and heterocycles as shown (**8**, **10**, and **11**). Different cleavage methods allow for the formation of acyclic or cyclic chiral constructs **8**-**11** that can then be used as synthons.



Scheme 2. *p*-Menthane-3-carboxaldehyde **5** as chiral auxiliary.

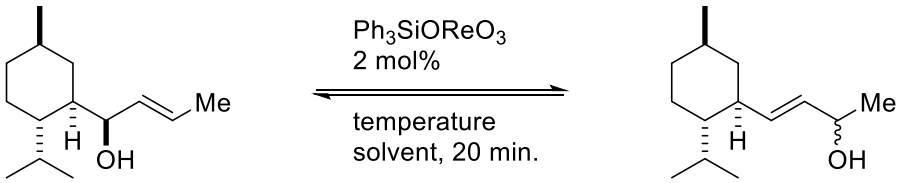
The large steric volume of the auxiliary is in part responsible for the high regioselectivity we observe when performing cuprate additions or rearrangement reactions on derivatives of **6**. We were intrigued to see if this steric bulk would be enough to bias the Re-catalyzed equilibrium between two regioisomeric hydroxyl groups **6** and **12** (Scheme 3). If so, we could significantly extend the usefulness of this method to making *O*-heterocycles **13**, cyclic alcohols **14**, α-hydroxy acids **15**, and other useful synthons.



Scheme 3. Possible use of Re(VII)-catalyzed isomerisation of alcohols **6** to access synthons **13-15**.

To test the idea, we submitted allylic alcohol **16a** to Osborn's catalyst[3] at 2 mol % loading under various reaction conditions. It was immediately apparent that the auxiliary was performing adequately in biasing the equilibrium between the two regioisomers **16a** and **17a** in favour of the latter (Table 1, entries 1 to 5). However, initially, complete epimerization of the stereocenter occurred (entry 1). It appeared that the Lewis acidity of the rhenium(VII) catalyst led to the formation of an allylic carbocation thereby destroying the stereochemical integrity of the system. Changing the solvent to toluene (entry 2) and ether (entry 3) improved this situation. We finally obtained a synthetically useful ratio of stereoisomers **17a** : **18a** by using ether at low temperature (entry 4). It is crucial to keep the temperature down (c.f. entry 5) and to limit the reaction time because the stereochemical integrity of the product erodes with time and side products start to appear. Dimeric ethers in particular form with time, sign that a carbocation is involved. In addition, water must be excluded from the medium because it slows the reaction considerably. Wet ether led only to traces of products in the same reaction time (entry 6). With these conditions found, we looked at the scope of the reaction.

Table 1. Optimization of the reaction condition of the Re-catalyzed transposition of allylic alcohol **16a**



16a **17a** β-OH
18a α-OH

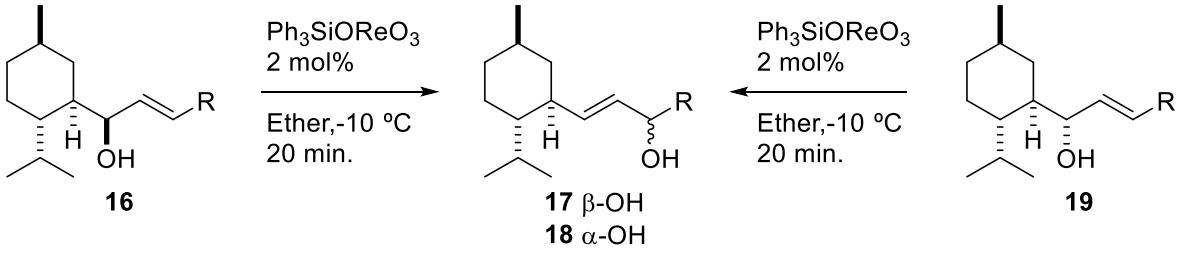
Entry	Temp. (°C)	Solvent	Yield[a] (%)	*rr* (**17a+18a : 16a**)	*dr* (**17a** : **18a**)
1	0	DCM	73	>95 : 5	50 : 50
2	0	PhMe	84	>95 : 5	78 : 22
3	0	Et_2O	82	>95 : 5	95 : 5
4	-10	Et_2O	81	>95 : 5	97 : 3
5	25	Et_2O	51	>95 : 5	71 : 29
6	0	Et_2O (wet)	0	-	-

a. Isolated yields of **17a** and **18a**.

Ratios of regioisomers were excellent across the board for different alkyl groups (Table 2, entries 1 to 10). We were happy to observe that even a *t*-butyl group cannot compete with the menthyl moiety for supremacy over the control of the equilibrium mixture of regioisomers (Table 2, entries 3 and 4). Notably, both stereoisomeric alcohols **16** and **19** could be successfully rearranged in a highly regioselective and stereospecific manner (entries 1 to 15, and 16-17). Of course, alcohols **16** and **19** led to an inverse ratio of the desired alcohols **17** and **18**, confirming the concerted nature of the rearrangement with conservation of stereochemical integrity.[1-3,17] Either starting alcohol **16** or **19** is easily obtained pure from menthylaldehyde,[16] which gives access to either stereochemistry of the desired product from the same enantiomer of the chiral auxiliary. Alternatively, the chiral auxiliary is also cheaply available in either configuration from the corresponding menthol.

A silyl-protected alcohol gave a high yield of the desired product (entries 13 and 14). Yet, protection of a spectator alcohol is not necessary, although a higher temperature and longer reaction time are required to reach equilibrium (entries 11 and 12). This is probably due to the competing formation of the rhenate ester with the spectator alcohol, so the yields of desired products **17f** and **18f** were lower, and some unidentified by-products were observed. The presence of an azide was also tolerated (entry 15), but the catalyst loading had to be increased to 10% otherwise the reaction was too slow and what we believe are nitrene-derived by-products started to appear.

Table 2. Scope of the Re-catalyzed transposition of allylic alcohols



Entry	Starting alcohol	R	Yield[a] (%)	*rr* (**17** : **16** or **18** : **19**)[c]	*dr* (**17** : **18**)[b]
1	**16a**	Me	81	> 98 : 2	97 : 3
2	**19a**	Me	Quant.	> 98 : 2	>2 : 98[c]
3	**16b**	*t*-Bu	Quant.	97 : 3	96 : 4
4	**19b**	*t*-Bu	Quant.	> 98 : 2	4 : 96
5	**16c**	Pent	Quant.	91 : 9	>99 : 1
6	**19c**	Pent	Quant.	> 98 : 2	10 : 90
7	**16d**	Bn	Quant.	> 98 : 2	> 99 : 1
8	**19d**	Bn	Quant.	> 98 : 2	> 1 : 99
9	**16e**	Cy	Quant.	> 98 : 2	>95 : 5[c]
10	**19e**	Cy	60	88 : 12	>5 : 95 [c]
11	**16f**	CH_2OH[d]	62[e]	> 98 : 2	> 95 : 5[c]
12	**19f**	CH_2OH[d]	54	> 98 : 2	> 5 : 95[c]
13	**16g**	CH_2OTBS	96	> 98 : 2	> 95 : 5[c]
14	**19g**	CH_2OTBS	68	> 98 : 2	> 5 : 95[c]
15	**16h**	$(CH_2)_3N_3$	80[f]	> 98 : 2	> 95 : 5[c]
16	**16i**	CF_3[g]	93	90 : 10	>95 : 5[c]
17	**19i**	CF_3[g]	66	90 : 10	>5 : 95[c]
18	**16j**	TMS[h]	---	---	---
19	**16k**	Ph	---	---	---

a. Isolated yields of **17** and **18**; b. Ratio determined by HPLC unless otherwise stated; c. Ratio determined by NMR; d. Room temp., 22 h.; e. Chromatography of the product was necessary; f. 10 mol % catalyst; g. Re_2O_7, DCE, reflux; h. THF, rt, 17 h.

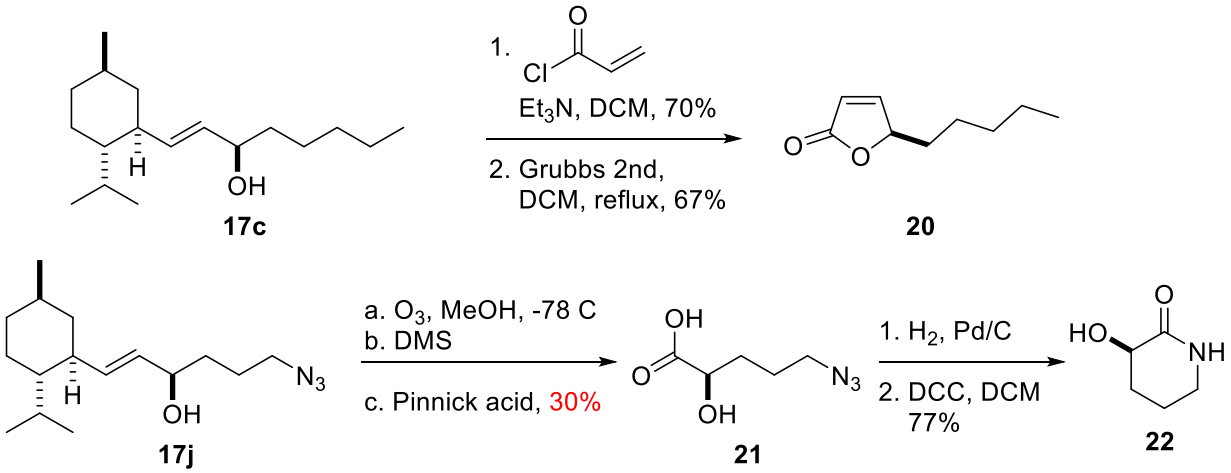
A trifluoromethyl gave a 9 : 1 regioisomeric ratio in favor of the desired regioisomers **17i** or **18i** (entries 16 and 17). This potent electron-withdrawing group renders the alcohol poorly nucleophilic and slows the

reaction down. The reaction took 1 h to reach equilibrium in refluxing dichloroethane. Despite the elevated temperature, the stereospecificity remained high. The strongly electron-withdrawing trifluoromethyl group undoubtedly prevents the formation of a carbocation, keeping the stereochemical integrity of the system intact even at 84 ºC. Compound **17i** was crystalline and a single crystal X-Ray diffraction analysis confirmed its structure. In addition, this X-ray confirmed the carbinol stereochemistry of **16i** (and hence, **19i**) because the mechanism of the rhenium(VII)-catalyzed rearrangement is known to be concerted.[3] The stereochemistry of **16** is expected from the Felkin-Anh model of addition to chiral aldehydes and we had prepared **16a-b** by this method.[16] Rearranging both isomers **16** and **19** allows us to ascertain the stereochemical purity of the products **17** and **18**. The stereochemistry of **17** and **18** was further confirmed by converting **17c** and **17j** to known compounds and measuring their optical rotation (*vide infra*).

The large trimethylsilyl group gave the starting regioisomer **16j** (entry 18) mixed with the epimerized product **19j**. This group is not only large but being electropositive, it prefers a sp^2 to a sp^3 carbon. Predictably, a conjugating group like phenyl (**16k**, entry 19) gave epimerization and no desired regioisomer **17k**.

As we had with our previous systems,[16] we envisaged cleaving the auxiliary in two main ways accessing useful synthons directly in the same step. We anticipated cleavage efficiencies to be similar to previous systems. Indeed, this was the case. The first example starts with the acylation of enantiomerically pure alcohol **17c** (Scheme 4). RCM cleavage of the resulting vinyl ester yielded furanone **20**. This compound has been successfully converted to cognac lactone by dimethylcuprate addition.[19] This is thus a 5-steps formal synthesis[20-23] of this prized natural aromatic oil[24] from 1-iodohept-1-ene.

The second example is the oxidative cleavage of alcohol **17j**. Ozonolysis and in situ oxidation supplied the chiral α-hydroxy acid **21**.[25] Chiral α-hydroxy acids are widely used synthons and are also used as depsi-peptides monomers.[26] We converted α-hydroxyacid **21** to lactam **22** by standard means and used this lactam to make the non-racemic version of a novel glycoside hydrolase inhibitor.[27]



Scheme 4. Cleavage of the auxiliary into useful synthons.

Conclusions

We have successfully extended our menthylaldehyde-based chiral auxiliary method to encompass secondary chiral allylic alcohols. Starting from alkynes, chiral non-racemic O-heterocycles and α-hydroxy acids can be

obtained regio- and stereospecifically in 3-5 steps. We are further expanding the method to access chiral non racemic tertiary alcohols. These are much trickier because of the easy formation of a carbocation and loss of stereochemical integrity. To the best of our knowledge, there are yet no example of a rhenium-catalyzed allylic rearrangement to make a chiral non-racemic tertiary allylic alcohol. We are designing a new chiral auxiliary to tackle this issue and will report the results in due course.

Experimental Section

General. All reactions were performed under an inert atmosphere of argon in glassware that had been flame-dried, or oven dried overnight. Solvents were distilled from lithium aluminum hydride (tetrahydrofuran, ether), sodium/benzophenone (toluene), calcium hydride (DCM, triethylamine) prior to use. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a 300 MHz Bruker spectrometer. NMR samples were dissolved in chloroform-*d* and chemical shifts are reported in ppm relative to the residual undeuterated solvent. Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, ddd = doublet of doublets of doublets, t = triplet, q = quartet, m = multiplet), coupling constant. Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a 75.5 MHz Bruker spectrometer. NMR samples were dissolved in chloroform-*d* and chemical shifts are reported in ppm relative to the solvent. High-resolution spectrometry was performed on a Shimadzu LC-QqTOF Nexera. Reactions were monitored by thin-layer chromatography (TLC) on *Silicycle* 0.25 mm silica gel coated glass plate UV 254, vanillin, $KMnO_4$, PMA, or by ^{1}H NMR. Silica gel (particule size: 230-400 mesh) was used for flash chromatography. Melting points are uncorrected.

Alcohols **16a, 16b, 16d, 16g, 16j, 16k, 19a, 19b, 19d, 19g, 19j, 19k** were prepared according to known procedures.[28-29]

(1*R*)-(*E*)-3-Cyclohexyl-1-(*p*-menthan-3-yl)prop-2-en-1-ol (16e) and (1*S*)-(*E*)-3-cyclohexyl-1-(*p*-menthan-3-yl)prop-2-en-1-ol (19e). (*E*)-(2-iodovinyl)cyclohexane (827 mg, 3.50 mmol) was dissolved in dry Et_2O (35 mL). This solution was cooled to -78 ºC and *t*-butyllithium (1.24 M in pentane, 5.64 mL, 7.0 mmol) was added dropwise. The reaction mixture was stirred at -78 ºC for 30 min and 2 h at rt. Then, the mixture was cooled again to -78 ºC and a solution of $AlMe_3$ (2.0 M in hexanes, 5.25 mL, 10.5 mmol) was added. Then, a solution of *p*-menthane-3-carboxaldehyde **5** (588 mg, 3.50 mmol) dissolved in Et_2O (5.0 mL) was added dropwise and the reaction mixture was stirred at -78 ºC for 2 h. The reaction mixture was then allowed to warm to 0 ºC and treated with a saturated solution of $NaHCO_3$ and stirred in a 1N aqueous solution of HCl until dissolution of the white solid. The aqueous phase was extracted with 3 portions of Et_2O and the combined organic extracts were washed once with water and once with brine, dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure to give a yellow oil (510 mg). The crude product was purified on silica gel with 5% ethyl acetate in hexanes as eluant to yield pure alcohol **16e** (245 mg, 25%), as well as pure alcohol **19e** (24 mg, 2%). Isomer **16e**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.52 (dq, 2H, *J* = 18.0, 5.9 Hz), 4.35 (d, 1H, *J* = 3.0 Hz), 2.13 (m, 1H), 1.96 (m, 2H), 1.78-1.58 (m, 8H), 1.38-1.19 (m, 6H), 1.17-0.78 (m, 5H), 0.92 (d, 3H, *J* = 8.9 Hz), 0.88 (d, 3H, *J* = 5.9 Hz), 0.76 (d, 3H, *J* = 6.1 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.6 (d), 129.7 (d), 71.5 (d), 44.8 (d), 43.1 (d), 40.4 (d), 35.2 (t), 33.1 (t), 33.0 (t), 32.8 (d), 26.3 (d), 26.2 (t), 26.1 (t), 24.3 (t), 22.9 (q), 21.6 (q), 15.5 (q). IR (neat) ν (cm^{-1}) 3347 (b), 2921, 1447. HRMS calcd for $C_{19}H_{34}O(Na^+)$: 301.2502, found: 301.2506. Isomer **19e**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.55 (dd, 2H, *J* = 3.8, 1.7 Hz), 4.35 (d, 1H, *J* = 4.5 Hz), 2.10-1.83 (m, 3H), 1.81-1.61 (m, 8H), 1.45-0.75 (m, 11H), 0.90 (d, 3H, *J* = 5.0 Hz), 0.87 (d, 3H, *J* = 5.3 Hz), 0.83 (d, 3H, *J* = 6.2). ^{13}C NMR (75 MHz,

$CDCl_3$) δ 136.7 (d), 131.5 (d), 72.7 (d), 48.4 (d), 40.3 (d), 39.9 (d), 36.8 (t), 36.0 (t), 32.8 (t), 32.7 (t), 29.0 (d), 27.9 (d), 26.2 (t), 26.1 (t), 26.0 (t), 23.2 (q), 21.8 (q), 21.7 (q). IR (neat) ν (cm^{-1}) 3387 (b), 2921, 1447. HRMS calcd for $C_{19}H_{34}O(Na^+)$: 301.2502, found: 301.2501.

(1*R*)-(*E*)-1-(*p*-Menthan-3-yl)but-2-en-1,4-diol (16 f) and (1*S*)-(*E*)-1-(*p*-menthan-3-yl)but-2-en-1,4-diol (19f). Propargyl alcohol (0.52 ml, 8.9 mmol) in dry THF (13 mL) was charged in a 50 mL oven-dried rb flask under argon. The solution was cooled at -78 °C and a solution of *t*-BuLi (2.5 M in hexanes, 7.14 mL, 17.8 mmol) was added dropwise. The reaction mixture was stirred during 1 h at that temperature and then *p*-menthyl-3-carboxaldehyde (**5**) (1.67 mL, 8.81 mmol) was added dropwise. The reaction mixture was stirred during 30 min. at -78 ºC after which time it was allowed to warm to rt and stirred a further 15 min. Then, 3N aq. HCl and diethyl ether were added to the reaction mixture. The phases were separated, and the aqueous phase was extracted with twice with diethyl ether. The organic phases were combined and washed with saturated aq. $NaHCO_3$ and brine. The resulting organic phase was dried with anhydrous $MgSO_4$ and concentrated under reduced pressure to yield the crude product as a colorless oil (1.80 g). The product was purified by flash chromatography on silica eluting with a mixture of hexanes and ethyl acetate (3:2) to yield the desired product as a mixture of diastereomers (1*S*)-1-(p-menthan-3-yl)but-2-yne-1,4-diol **23** and (1*R*)-1-(p-menthan-3-yl)but-2-yne-1,4-diol **24** (1.16 g, 57%). A small fraction was chromatographed for the sole purpose of characterization because separation of the isomers is much easier at the alkene stage (**16f** from **19f**). Isomer **23**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.74 (q, 1H, *J* = 2.0 Hz), 4.34 (m, 2H), 2.12-1.59 (m, 7H), 1.57-1.25 (m, 3H), 1.1-0.80 (m, 2H), 0.94 (d, 6H, *J* = 7.0 Hz), 0.78 (d, 3H, *J* = 6.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 86.8 (s), 83.9 (s), 62.8 (d), 51.3 (t), 44.9 (d), 42.8 (d), 35.2 (t), 34.9 (t), 32.9 (d), 26.2 (d), 24.2 (t), 22.9 (q), 21.6 (q), 15.6 (q). IR (neat) ν (cm^{-1}) 3300 (b), 2954, 1452. HRMS calcd for $C_{14}H_{24}O_2(Na^+)$: 247.1669, found: 247.1674. Isomer **24**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.70 (bs, 1H), 4.32 (m, 2H), 1.95-1.80 (m, 2H), 1.78-1.56 (m, 4H), 1.57-0.70 (m, 6H), 0.93 (d, 3H, *J* = 6.9 Hz), 0.90 (d, 3H, *J* = 6.8 Hz), 0.78 (d, 3H, *J* = 6.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 84.8 (s), 84.5 (s), 63.6 (d), 51.4 (t), 44.6 (d), 44.3 (d), 35.1 (t), 34.4 (t), 32.3 (d), 26.7 (d), 24.1 (t), 22.9 (q), 21.6 (q), 15.5 (q). IR (neat) ν (cm^{-1}) 3245 (b), 2947, 1455. HRMS calcd for $C_{14}H_{24}O_2(Na^+)$: 247.1669, found: 247.1674.

To a stirring solution of Red-Al (60% in toluene, 1.16 mL, 3.57 mmol) in THF (5.2 mL) at 0 °C was added a mixture of propargylic alcohols **23** and **24** (200 mg, 0.89 mmol). After stirring for 75 min at that temperature, the reaction was quenched with 3 N HCl and extracted with AcOEt three times. The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure to yield the crude product as a light brown oil (196 mg). The crude product was purified by flash chromatography on silica eluting with a mixture of hexanes and ethyl acetate (3:2) to yield three fractions: 64 mg (32%) of pure **16f**, 83 mg (41%) of a mixture of both and 29 mg (14%) of pure **19f** for a total of 176 mg (87%). Isomer **16f**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.83 (m, 2H), 4.48 (m, 1H), 4.20 (m, 2H), 2.13 (m, 1H), 1.98-1.44 (m, 3H), 1.45-1.18 (m, 4H), 1.10-0.66 (m, 4H), 0.94 (d, 3H, *J* = 6.9 Hz), 0.88 (d, 3H, *J* = 6.4 Hz), 0.77 (d, 3H, *J* = 6.9 Hz**).** ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.4 (d), 139.0 (d), 70.8 (d), 63.3 (t), 44.6 (d), 43.1 (d), 35.3 (t), 33.8 (t), 32.9 (d), 26.5 (d), 24.5 (t), 22.9 (q), 21.7 (q), 15.6 (q). IR (neat) ν (cm^{-1}) 3343 (b), 2952, 2916, 1454. HRMS calcd for $C_{14}H_{26}O_2(Na^+)$: 249.1825, found: 249.1830. Isomer **19f**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.87 (dt, 1H, *J* = 18.0, 5.8 Hz), 5.79 (dd, 1H, *J* = 18.0, 6.0 Hz), 4.48 (m, 1H), 4.19 (m, 2H), 1.95 (m, 1H), 1.85 (m, 1H), 1.76-1.52 (m, 2H), 1.46-1.19 (m, 4H), 1.08-0.58 (m, 4H), 0.89 (d, 3H, *J* = 6.9 Hz), 0.88 (d, 3H, *J* = 6.8 Hz), 0.80 (d, 3H, *J* = 6.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 130.8 (d), 130.7 (d), 71.5 (d), 63.4 (t), 45.0 (d), 44.1 (d), 35.3 (t), 34.1 (t), 32.6 (d), 26.5 (d), 24.4 (t), 22.9 (q), 21.6 (q), 15.4 (q). IR (neat) ν (cm^{-1}) 3291 (b), 2956, 2914, 1455. HRMS calcd for $C_{14}H_{26}O_2(Na^+)$: 249.1825, found: 249.1833.

(1*R*)-(*E*)-4-(t-Butyldimethylsilyloxy)-1-(*p*-menthan-3-yl)but-2-en-1-ol (16g) and (1*S*)-(*E*)-4-(t-butyldimethyl-silyloxy)-1-(*p*-menthan-3-yl)but-2-en-1-ol (19g). A 1:2 mixture of the starting diols **16f** and **19f** (214 mg, 945 µmol) was dissolved in DCM (5 mL) and the solution was cooled to 0 °C. Imidazole (84 mg, 1.22 mmol) and TBSCl (157 mg, 1.04 mmol) were added, and the reaction mixture was stirred at rt for 45 min. Water and DCM were added to the reaction mixture and the phases were separated. The aqueous phase was extracted 3 times with DCM. The combined organic phases were washed with water and then brine. The resulting organic phase was dried with anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure to yield the crude product as a colorless oil (318 mg). The product was purified by flash chromatography on silica eluting with a mixture of hexanes and ethyl acetate (9:1) to yield pure TBS ether **16g** (83 mg, 26%), as well as pure TBS ether **19g** (138 mg, 43%) and a mixed fraction (59 mg, 18%). Isomer **16g**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.75 (m, 2H), 4.45 (bs, 1H), 4.21 (m, 2H), 2.12 (m, 1H), 1.75-1.50 (m, 3H), 1.40-1.20 (m, 4H), 1.09-0.74 (m, 3H), 0.93 (d, 3H, *J* = 6.9 Hz), 0.92 (s, 9H), 0.87 (d, 3H, *J* = 6.4 Hz), 0.77 (d, 3H, *J* = 6.9 Hz), 0.08 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 132.7 (d), 129.2 (d), 70.9 (d), 63.4 (t), 44.6 (d), 43.0 (d), 35.2 (t), 33.8 (t), 32.8 (d), 26.3 (d), 26.0 (q), 24.3 (t), 22.8 (q), 21.5 (q), 18.5 (s), 15.5 (q), -5.1 (q), -5.2 (q). **IR** (neat) ν (cm^{-1}) 3400 (b), 2952, 2927, 1462. HRMS calcd for $C_{20}H_{40}O_2Si(Na^+)$: 363.2688, found: 363.2692. Isomer **19g**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.77 (m, 2H), 4.46 (bs, 1H), 4.20 (m, 2H), 1.94 (m, 1H), 1.85 (m, 1H), 1.75-150 (m, 4H), 1.46-1.21 (m, 2H), 1.09-0.74 (m, 3H), 0.92 (s, 9H), 0.89 (d, 3H, *J* = 6.9 Hz), 0.87 (d, 3H, *J* = 6.4 Hz), 0.79 (d, 3H, *J* = 6.9 Hz), 0.08 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 131.0 (d), 128.9 (d), 71.4 (d), 63.3 (t), 44.7 (d), 44.0 (d), 35.2 (t), 33.9 (t), 32.5 (d), 26.3 (d), 25.9 (q), 24.2 (t), 22.8 (q), 21.4 (q), 18.4 (s), 15.2 (q), -5.1 (q), -5.2 (q). IR (neat) ν (cm^{-1}) 3376 (b), 2952, 2928, 1461. HRMS calcd for $C_{20}H_{40}O_2Si(Na^+)$: 363.2688, found: 363.2695.

(1*R*)-(*E*)-6-Azido-1-(*p*-menthan-3-yl)hex-2-en-1-ol (16h). To a clear colorless solution of *E*-5-*t*-butyldimethylsilyloxy-1-iodopent-1-ene **25** (6.36 g, 19.5 mmol) in Et_2O (66 mL) under argon was added at -78 °C a solution of *n*-BuLi in hexanes (6.96 mL, 2.8 M, 19.5 mmol) over 5 min. The clear pale yellow reaction mixture was stirred for 2h and allowed to warm to rt for 30 min. It was cooled down to -78 ºC and a solution of trimethylaluminium (2 M in toluene, 24.0 mL, 48.7 mmol) was slowly added, followed by a solution of (-)-*p*-menthane-3-carboxaldehyde **5** (3.28 g, 19.5 mmol) in Et_2O (30 mL). The reaction mixture was stirred overnight while letting the dry ice/acetone bath slowly warm to rt. It was then cooled to 0 °C, and a minimum amount of saturated aqueous solution of $NaHCO_3$ was slowly added until gas evolution stopped, and a white precipitate formed. Then the solution was acidified with 1 N aqueous HCl and the mixture was stirred until no more gas formation was observed. Finally, aqueous 3 N HCl was added to help solubilize the solids and the aqueous phase was extracted with diethyl ether. The organic layers were combined, washed with saturated aqueous $NaHCO_3$ and with brine. The organic phase was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure to yield the crude product as a colorless oil (8.3 g). The crude product was purified by flash chromatography eluting with a gradient of hexanes and ethyl acetate (9:1 to 8:2) to yield the pure desired (1*R*)-(*E*)-6-(*t*-butyldimethylsilyloxy)-1-(*p*-menthan-3-yl)hex-2-en-1-ol (**26**) as a colorless oil (3.94 g, 80%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.70-5.49 (m, 1H), 4.38 (d, 1H, *J* = 4.9 Hz), 3.62 (t, 1H, *J* = 6.4 Hz), 2.12 (q, 2H, *J* = 6.8 Hz), 1.75-1.50 (m, 4H), 1.42-1.19 (m ,5H), 0.93 (d, 1H, *J* = 6.9 Hz), 0.90 (s, 9H), 0.89 (d, 3H, *J* = 6.7 Hz), 0.76 (d, 3H, *J* = 6.9 Hz), 0.05 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 132.6 (d), 130.3 (d), 71.4 (d), 62.6 (t), 44.8 (d), 43.0 (d), 35.2 (t), 33.8 (t), 32.8 (d), 29.4 (d), 28.6 (t), 26.3 (d), 26.0 (q), 24.3 (t), 22.9 (q), 21.6 (q), 15.5 (q), -5.3 (q). IR (neat) ν (cm^{-1}) 3409 (b), 2951, 1462. HRMS calcd for $C_{22}H_{44}O_2Si(Na^+)$: 391.3003, found: 391.3003.

Silyl ether **26** (1.39g, 3.77 mmol) was dissolved in dry THF (15.0 mL mL) at rt under argon. TBAF (1.0 M in THF, 4.15 mL, 4.15 mmol) was added and the reaction mixture was stirred during 3.5 h. Saturated aqueous NH_4Cl was added to the reaction mixture and the THF was removed under reduced pressure. Diethyl ether was

added, and the phases were separated. The aqueous phase was extracted three times with diethyl ether and the organic phases were combined. The resulting organic phase was washed once with brine, dried with anhydrous magnesium sulfate and filtered through paper filter. The filtrate was concentrated under reduced pressure and dried under vacuum to yield the crude product as a colorless oil (1.28 g). The crude product was purified by flash chromatography eluting with a mixture of hexanes and ethyl acetate (3:7) to yield the desired (1*R*)-(*E*)-1-(*p*-menthan-3-yl)hex-2-en-1,6-diol **27** as a colorless oil (950 mg, 99%). The product contained an impurity which was difficult to remove and was used as is in the next reaction. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.69-5.56 (m, 2H), 4.38 (m, 1H), 3.67 (t, 2H, *J* = 6.5 Hz), 2.24-2.06 (m, 2H), 1.84-1.49 (m, 5H), 1.45-1.13 (m, 5H), 1.11-0.58 (m, 4H), 0.93 (d, 3H, *J* = 6.9 Hz), 0.88 (d, 3H, *J* = 6.9 Hz), 0.76 (d, 3H, *J* = 6.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 133.1 (d), 130.0 (d), 71.4 (d), 62.6 (t), 44.9 (d), 43.2 (d), 35.3 (t), 34.0 (t), 32.9 (d), 32.4 (t), 28.8 (t), 26.5 (d), 24.5 (t), 23.0 (q), 21.7 (q), 15.6 (q). IR (neat) ν (cm^{-1}) 3339 (b), 2954, 2923, 1448. HRMS calcd for $C_{16}H_{30}O_2(Na^+)$: 277.2138, found: 277.2139.

Diol **27** (167 mg, 0.656 mmol) was suspended in dry THF (3.1 mL) under an atmosphere of argon. Triphenylphosphine (181 mg, 0.689 mmol) and a solution of HN_3 (0.28 M in benzene, 3.3 mL, 0.92 mmol) were added to the suspension, which had been cooled to 0 °C, followed by the dropwise addition of diisopropylazodicarboxylate (DIAD, 136 µL, 0.689 mmol). Subsequently the reaction mixture was allowed to warm to rt and stirred overnight. The reaction mixture was concentrated under reduced pressure. The resulting residue was dissolved in minimal amount of CH_2Cl_2 and washed with H_2O and brine. The combined organic phases were dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure to yield the crude product as a yellow oil (509 mg). The crude product was purified by flash chromatography eluting with a mixture of hexanes and ethyl acetate (80:20) to yield the pure desired (1*R*,)-(*E*)-6-azido-1-(*p*-menthan-3-yl)hex-2-en-1-ol (**16h**) as a clear oil (140 mg, 77%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.59 (m, 2H), 4.40 (bs, 1H), 3.29 (t, 2H, *J* = 6.8 Hz), 2.25-2.03 (m, 3H), 1.75-1.55 (m, 5H), 1.41-1.17 (m, 4H), 1.11-0.70 (m, 3H), 0.93 (d, 3H, *J* = 6.9 Hz), 0.88 (d, 3H, *J* = 6.7 Hz), 0.76 (d, 3H, *J* = 6.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 133.9 (d), 128.8 (d), 71.3 (d), 51.0 (t), 44.8 (d), 43.2 (d), 35.3 (t), 33.9 (t), 32.9 (d), 29.5 (t), 28.6 (t), 26.5 (d), 24.4 (t), 22.9 (q), 21.5 (q), 15.5 (q). IR (neat) ν (cm^{-1}) 3398 (bs), 2949, 2916, 2092(s), 1453. HRMS calcd for $C_{16}H_{29}N_3O(Na^+)$: 302.2203, found: 302.2208.

(1*R*)-(*E*)-1-Trifluoromethyl-4-(*p*-menthan-3-yl)prop-2-en-1-ol (16i) and (1*S*)-(*E*)-1-trifluoromethyl-4-(*p*-menthan-3-yl)prop-2-en-1-ol (19i). A small crystal of triphenylmethane was dissolved in dry THF (30 mL) under argon. The solution was cooled to -56 °C (octane bath) and 2.5 M *n*-BuLi in hexanes (4.25 mL, 10.6 mmol) was added resulting in a pink solution. 3,3,3-Trifluoroprop-1-yne gas was gently bubbled through the solution until the disappearance of the pink color (4.7 g, 50 mmol). Note that the solution starts to get darker after less than 5 min. Then, *p*-menthyl-3-carboxaldehyde **5** (2.19 mL, 11.7 mmol) was added and the reaction mixture was stirred at that temperature for 15 min. The solution was then warmed to rt. Saturated aqueous ammonium chloride and diethyl ether were added and the phases were separated. The aqueous phase was extracted three times with diethyl ether. The combined organic phases were washed with water twice and with brine once. The organic phase was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure to yield the crude product as a light brown oil (3.06 g). The crude product was purified by flash chromatography on silica eluting with a mixture of hexanes and ethyl acetate (95:5) to yield the pure major diastereoisomer (1*S*)-(*E*)-4-(*p*-menthan-3-yl)-1-trifluoromethylprop-2-yn-1-ol **28** of the desired product as clear oil (1.11 g, 40%). The pure minor diastereoisomer (1*R*)-1-trifluoromethyl-4-(*p*-menthan-3-yl)prop-2-yn-1-ol **29** was obtained as clear oil (81 mg, 3%). Also, a mixture of the major and minor diastereomers was obtained in about 1:2 ratio as oil (882 mg, 32%). Diastereomer **28** : ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.76 (m, 1H), 2.07-1.21 (m, 7H), 1.10-0.80 (m, 6H), 0.94 (d, 3H, *J* = 6.7 Hz), 0.93 (d, 3H, *J* = 6.9 Hz), 0.77 (d, 3H, *J* = 6.9 Hz). **^{13}C**

NMR (75 MHz, $CDCl_3$) δ 114.2 (q), 88.2 (q), 72.6 (s), 62.5 (d), 44.5 (d), 42.7 (d), 35.0 (t), 34.9 (t), 32.8 (d), 26.8 (d), 24.1 (t), 22.8 (q), 21.5 (q), 15.6 (q). ^{19}F NMR (285 MHz, $CDCl_3$) δ -50.18 (d, *J* = 3.6 Hz). IR (neat) ν (cm^{-1}) 3373 (b), 2957, 2256, 1207 (s), 1134 (s). HRMS calcd for $C_{14}H_{23}F_3O(Na^+)$: 285.1437, found: 285.1440. Diastereomer **29** : ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.75 (m, 1H), 2.06-1.60 (m, 7H), 1.44-0.75 (m, 6H), 0.94 (d, 3H, *J* = 6.7 Hz), 0.92 (d, 3H, *J* = 6.9 Hz), 0.79 (d, 3H, *J* = 6.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 114.2 (q), 86.6 (q), 72.6 (s), 63.5 (d), 44.3 (d), 44.2 (d), 34.9 (t), 34.6 (t), 32.3 (d), 26.9 (d), 24.0 (t), 22.7 (q), 21.5 (q), 15.5 (q). ^{19}F NMR (285 MHz, $CDCl_3$) δ -50.17 (d, *J* = 3.1 Hz). IR (neat) ν (cm^{-1}) 3337 (b), 2957, 2259, 1268 (s), 1135 (s). HRMS calcd for $C_{14}H_{23}F_3O$ (M^+-HO): 245.1512, found: 245. 1512.

To a stirring solution of Red-Al (60% in toluene, 1.76 mL, 5.44 mmol) in toluene (5.5 mL) at -78 °C was added the above trifluoropropargylic alcohol **28** (0.95 g, 3.60 mmol). After stirring for 1.5 h at that temperature, the reaction was quenched with 3 N HCl and extracted with AcOEt three times. The organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure to yield the crude product as a light brown oil (920 mg). The crude product was purified by flash chromatography on silica eluting with a mixture of hexanes and ethyl acetate (95:05) to yield the pure desired product **16i** as clear oil (850 mg, 89%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.38 (dm, 1H, *J* = 15.4 Hz), 5.92 (dqd, 1H, *J* = 15.4, 6.6, 2.2 Hz), 4.60 (m, 1H), 2.04 (m, 1H), 1.72 (m, 2H), 1.53-1.18 (m, 5H), 1.11-0.74 (m, 3H), 0.95 (d, 3H, *J* = 6.9 Hz), 0.89 (d, 3H, *J* = 6.4 Hz), 0.78 (d, 3H, *J* = 6.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.8 (q), 123.3 (q), 117.9 (q, *J* = 33.8 Hz), 69.3 (d), 43.7 (d), 42.9 (d), 35.0 (t), 33.6 (t), 32.6 (d), 26.5 (d), 24.2 (t), 22.7 (q), 21.4 (q), 15.4 (q). ^{19}F NMR (285 MHz, $CDCl_3$) δ -63.6 (dt, *J* = 6.7, 2.7 Hz). IR (neat) ν (cm^{-1}) 3448 (b), 2955, 1456. HRMS calcd for $C_{14}H_{22}F_3$ (M^+-HO): 247.1668, found: 247.1669.

The same procedure as per **16i**, starting from alcohol **29**, yielded 31% of product **19i** (along with 21% of a mixture of isomers that was not further purified). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.43 (dm, 1H, *J* = 15.7 Hz), 5.92 (dqd, 1H, *J* = 15.7, 6.5, 2.0 Hz), 4.62 (m, 1H), 2.02-1.63 (m, 5H), 1.45-1.23 (m, 2H), 1.17-0.76 (m, 3H), 0.95 (d, 3H, *J* = 6.9 Hz), 0.92 (d, 3H, *J* = 6.6 Hz), 0.84 (d, 3H, *J* = 6.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.4 (q), 123.3 (q), 118.9 (q, *J* = 33.7 Hz), 69.7 (d), 45.1 (d), 44.0 (d), 34.9 (t), 34.1 (t), 32.4 (d), 26.6 (d), 24.3 (t), 22.6 (q), 21.4 (q), 15.2 (q). ^{19}F NMR (285 MHz, $CDCl_3$) δ -63.7 (dt, *J* = 6.6, 2.5 Hz). IR (neat) ν (cm^{-1}) 3364 (b), 2957, 1456. HRMS calcd for $C_{14}H_{23}F_3O$ (M^+-HO): 247.1668, found: 247.1668.

General procedure B for Re(VII)-catalyzed rearrangements of alcohols 16 or 19

In a glove box under argon, trioxo(triphenylsiloxy)rhenium(VII) (2 mol%) was added in a 5 mL oven-dried rb flask equipped with a magnetic stir bar. The flask was closed with a septum, removed from the glove box and plugged into an argon line. Dry diethyl ether (0.4 M) was added. The resulting solution was added to a solution of the alcohol 12 or 15 in dry diethyl ether (0.4 M so that the total concentration was 0.2 M) at -10 ºC and the reaction mixture was stirred for 20 min unless otherwise stated. Triethylamine (15 mol%) was added to the red reaction mixture. The resulting white suspension was filtered through a silica pad and concentrated under reduced pressure to obtain the crude product.

(2*R*)-(*E*)-4-(*p*-Menthan-3-yl)but-3-en-2-ol (17a). Done according to the general procedure B. 52 mg (81%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.44 (ABdd, 2H), 4.26 (p, 1H, *J* = 6.3 Hz), 2-1.5 (m, 5H), 1.5-1.27 (m, 2H), 1.25 (d, 3H, *J* = 6.3 Hz), 1.1-0.75 (m, 4H), 0.86 (d, 6H, *J* = 6.8 Hz), 0.70 (d, 3H, *J* = 6.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.9 (d), 133.4 (d), 69.2 (d), 47.3 (d), 44.3 (d), 43.2 (t), 35.3 (t), 32.6 (d), 28.2 (d), 24.3 (t), 23.7 (q), 22.7 (q), 21.6 (q), 15.5 (q). IR (neat) ν (cm^{-1}) 3350 (b), 2918, 1434. HRMS calcd for $C_{14}H_{26}O(Na^+)$: 233.1876, found: 233.1878.

(3*S*)-(*E*)-5-(*p*-Menthan-3-yl)-2,2-dimethylpent-4-en-3-ol (17b). Done according to the general procedure B. 94 mg (91%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.64 (dd, 1H, *J* = 15.8, 1.3 Hz), 5.43 (dd, 1H, *J* = 15.8, 5.6 Hz), 4.37 (bt, 1H), 2.14 (qt, 1H, *J* = 6.9, 3.6 Hz), 1.75-1.5 (m, 4H), 1.4-1.1 (m, 4H), 1.03 (s, 9H), 1.0-0.7 (m, 2H), 0.93 (d, 3H, *J* = 6.9 Hz), 0.88 (d, 3H, *J* = 6.5 Hz), 0.77 (d, 3H, *J* = 6.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.8 (d), 127.0 (d), 71.7 (d),

45.0 (d), 43.3 (d), 35.3 (t), 34.0 (t), 33.0 (s), 32.9 (d), 29.4 (q), 26.5 (d), 24.5 (t), 23.0 (q), 21.7 (q), 15.7 (q). IR (neat) ν (cm^{-1}) 3369 (b), 2951, 1456**.** HRMS calcd for $C_{17}H_{32}O(Na^+)$: 275.2345, found: 275.2348.

(6*R*)-(*E*)-8-(*p*-Menthan-3-yl)oct-7-en-6-ol (17c). Done according to the general procedure B. 68 mg (68%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.42 (m, 2H), 4.04 (m, 1H), 1.97-1.20 (m, 12H), 1.1-0.65 (m, 8H), 0.87 (d, 6H, *J* = 7.5 Hz), 0.71 (d, 3H, *J* = 6.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.2 (d), 132.2 (d), 73.4 (d), 47.1 (d), 44.4 (d), 43.1 (t), 37.4 (t), 35.2 (t), 32.4 (d), 31.7 (t), 28.08 (d), 25.2 (t), 24.0 (t), 22.7 (t), 22.6 (q), 24.4 (q), 15.2 (q), 14.0 (q). IR (neat) ν (cm^{-1}) 3334 (b), 2953, 1455. HRMS calcd for $C_{17}H_{32}O(Na^+)$: 289.2502, found: 289.2510.

(2*R*)-(*E*)-4-(*p*-Menthan-3-yl)-1-phenylbut-3-en-2-ol (17d). Done according to the general procedure B. 68 mg (68%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35-7.10 (m, 5H), 5.43 (ABdd, 2H), 4.33 (q, 1H, *J* = 6.7 Hz), 2.86 (ABdd, 2H), 1.89 (m, 1H), 1.8-1.28 (m, 7H), 1.1-0.75 (m, 3H), 0.90 (d, 3H, *J* = 6.5 Hz), 0.82 (d, 3H, *J* = 7.0 Hz), 0.68 (d, 3H, *J* = 6.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.9 (s), 137.7 (d), 131.0 (d), 129.6 (d), 128.3 (d), 126.3 (d), 74.1 (d), 47.0 (d), 44.4 (d), 44.2 (t), 43.1 (t), 35.2 (t), 32.4 (d), 27.8 (d), 24.0 (t), 22.6 (q), 21.4 (q), 15.3 (q). IR (neat) ν (cm^{-1}) 3251 (b), 2957, 2925, 1455. HRMS calcd for $C_{20}H_{30}O(Na^+)$: 309.2189, found: 309.2193.

(1*S*)-(*E*)-1-Cyclohexyl-3-(*p*-menthan-3-yl)prop-2-en-1-ol (17e). Done according to the general procedure B. 182 mg (82%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.48 (m, 2H), 3.77 (td, 1H, *J* = 6.3, 3.7 Hz), 1.97-1.52 (m, 11H), 1.46-1.08 (m, 6H), 1.03-0.76 (m, 50.87 (d, 6H, *J* = 6.8 Hz), 0.71 (d, 3H, *J* = 6.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.9 (d), 130.6 (d), 77.7 (d), 47.1 (d), 44.7 (d), 43.8 (d), 43.2 (t), 35.2 (t), 32.5 (d), 28.8 (t) , 28.7 (t), 28.1 (d) , 26.6 (t), 26.2 (t), 26.1 (t), 24.0 (t), 22.6 (q), 21.4 (q), 15.2 (q). IR (neat) ν (cm^{-1}) 3298 (b), 2953, 1451. HRMS calcd for $C_{19}H_{34}O(Na^+)$: 301.2502, found: 301.2506.

(2*S*)-(*E*)-4-(*p*-Menthan-3-yl)but-3-en-1,2-diol (17f). Done according to the general procedure B. 47 mg (62%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.57 (dd, 1H, *J* = 15.5, 9.0 Hz), 5.41 (dd, 1H, *J* = 15.5, 6.3 Hz), 4.21 (m, 1H), 3.63 (ddd, 1H, *J* = 11.5, 7.0, 3.6 Hz), 3.48 (ddd, 1H, *J* = 11.5, 7.5, 4.8 Hz), 2.0-1.5 (m, 7H), 1.45-1.23 (m, 1H), 1.1-0.75 (m, 4H), 0.87 (d, 6H, *J* = 6.8 Hz), 0.70 (d, 3H, *J* = 6.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.1 (d), 127.3 (d), 73.2 (d), 66.7 (t), 47.0 (d), 44.4 (d), 43.0 (t), 35.1 (t), 32.4 (d), 28.4 (d), 24.1 (t), 22.6 (q), 21.4 (q), 15.3 (q). IR (neat) ν (cm^{-1}) 3353 (b), 2951, 1454. HRMS calcd for $C_{14}H_{26}O_2(Na^+)$: 249.1825, found: 249.1832.

(2*S*)-(*E*)-1-(*t*-Butyldimethylsilyloxy)-4-(*p*-menthan-3-yl)but-3-en-2-ol (17g). Done according to the general procedure B. 109 mg (84%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.53 (dd, 1H, *J* = 15.5, 8.9 Hz), 5.37 (dd, 1H, *J* = 15.5, 6.4 Hz), 4.10 (m, 1H), 3.61 (dd, 1H, *J* = 9.9, 3.8 Hz), 3.42 (dd, 1H, *J* = 9.9, 7.5 Hz), 2.48 (d, 1H, *J* = 3.3 Hz), 1.99-1.5 (m, 5H), 1.46-1.26 (m, 1H), 1.05-0.76 (m, 4H), 0.90 (s, 9H), 0.86 (d, 6H, *J* = 6.8 Hz), 0.69 (d, 3H, *J* = 6.9 Hz), 0.08 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.4 (d), 127.3 (d), 72.8 (d), 67.3 (t), 47.0 (d), 44.4 (d), 43.0 (t), 35.1 (t), 32.4 (d), 28.0 (d), 25.9 (q), 24.1 (t), 22.6 (q), 21.4 (q), 18.3 (s), 15.3 (q), -5.3 (q), -5.4 (q). IR (neat) ν (cm^{-1}) 3407 (b), 2952, 1462. HRMS calcd for $C_{20}H_{40}O_2Si(Na^+)$: 363.2690, found: 363.2694.

(4*R*)-(*E*)-1-Azido-6-(*p*-menthan-3-yl)hexen-5-en-4-ol (17h). Done according to the general procedure B. 140 mg (76%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.59 (m, 2H), 4.40 (m, 1H), 3.29 (t, 2H, *J* = 6.8 Hz), 2.23-2.03 (m, 3H), 1.76-1.55 (m, 4H), 1.41-1.14 (m, 4H), 1.09-0.68 (m, 4H), 0.93 (d, 3H, *J* = 6.9 Hz), 0.88 (d, 3H, *J* = 6.4 Hz), 0.76 (d, 3H, *J* = 6.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 133.9 (d), 128.8 (d), 71.3 (d), 51.0 (t), 44.8 (d), 43.2 (d), 35.3 (t), 34.0 (t), 32.9 (d), 29.5 (t), 28.6 (t), 26.5 (d), 24.4 (t), 23.0 (q), 21.7 (q), 15.6 (q). IR (neat) ν (cm^{-1}) 3398 (b), 2949, 2092, 1453. HRMS calcd for $C_{16}H_{29}ON_3(Na^+)$: 302.2203, found: 302.2208.

(1*S*)-(*E*)-1-Trifluoromethyl-4-(*p*-menthan-3-yl)-prop-2-en-1-ol (17i). Done according to the general procedure B. 33 mg (66%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.76 (dd, 1H, *J* = 15.5, 9.1 Hz), 5.48 (dd, 1H, *J* = 15.5, 6.9 Hz), 4.39 (sextet, 1H, *J* = 6.9 Hz), 2.09-1.93 (m, 2H), 1.80-1.68 (m, 2H), 1.51-1.24 (m, 2H), 1.10-0.75 (m, 5H), 0.88 (d, 3H, *J* = 7.0 Hz), 0.87 (d, 3H, *J* = 7.1 Hz), 0.71 (d, 3H, *J* = 6.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.9 (d), 121.2 (d), [$\underline{C}F_3$ = 130.1, 126.4, 122.7, 118.9], [$\underline{C}H$-CF_3 = 72.5, 72.1, 71.7, 71.2], 47.1 (d), 44.7 (d), 42.6 (t), 35.2 (t), 32.5 (d), 28.3

(d), 24.2 (t), 22.7 (q), 21.5 (q), 15.4 (q). ^{19}F NMR (285 MHz, $CDCl_3$) δ -79.55 (d, 3F, *J* = 9 Hz). IR (neat) ν (cm^{-1}) 3308 (b), 1456. HRMS calcd for $C_{14}H_{23}OF_3(Na^+)$: 287.1593, found: 287.1594.

(2*S*)-(*E*)-4-(*p*-Menthan-3-yl)but-3-en-2-ol (18a). Done according to the general procedure B. 99 mg (99%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.47 (ABdd, 2H), 4.26 (qd, 1H, *J* = 6.2, 3.5 Hz), 2.0-1.5 (m, 5H), 1.5-1.3 (m, 2H), 1.27 (d, 3H, *J* = 6.3 Hz), 1.1-0.75 (m, 4H), 0.90 (d, 3H, *J* = 6.8 Hz), 0.89 (d, 6H, *J* = 6.8 Hz), 0.73 (d, 3H, *J* = 6.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.0 (d), 133.4 (d), 69.2 (d), 47.3 (d), 44.2 (d), 43.3 (t), 35.3 (t), 32.6 (d), 28.2 (d), 24.2 (t), 23.6 (q), 22.7 (q), 21.6 (q), 15.5 (q). IR (neat) ν (cm^{-1}) 3330 (b), 2952, 2915, 1455. HRMS calcd for $C_{14}H_{26}O(Na^+)$: 233.1876, found: 233.1880.

(3*R*)-(*E*)-5-(*p*-Menthan-3-yl)-2,2-dimethylpent-4-en-3-ol (18b). Done according to the general procedure B. 69 mg (99%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.48 (ABdd, 2H), 3.72 (bd, 1H, *J* = 5.8 Hz), 2.05-1.5 (m, 5H), 1.4-1.1 (m, 4H), 0.92 (s, 9H), 1.0-0.7 (m, 8H), 0.74 (d, 3H, *J* = 6.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.2 (d), 129.0 (d), 81.1 (d), 47.3 (d), 44.7 (d), 43.5 (t), 35.3 (t), 35.1 (s), 32.6 (d), 28.3 (d), 25.9 (q), 24.2 (t), 22.8 (q), 21.6 (q), 15.5 (q). IR (neat) ν (cm^{-1}) 3393 (b), 2952, 2914, 1455. HRMS calcd for $C_{17}H_{32}O(Na^+)$: 275.2345, found: 275.2348.

(6*S*)-(*E*)-8-(*p*-Menthan-3-yl)oct-7-en-6-ol (18c). Done according to the general procedure B. 55 mg (74%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.45 (m, 2H), 4.06 (m, 1H), 2.0-1.2 (m, 12H), 1.1-0.65 (m, 8H), 0.89 (d, 6H, *J* = 7.5 Hz), 0.73 (d, 3H, *J* = 6.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.7 (d), 132.2 (d), 73.2 (d), 47.2 (d), 44.2 (d), 43.2 (t), 37.3 (t), 35.2 (t), 32.5 (d), 31.8 (t), 28.1 (d), 25.1 (t), 24.1 (t), 22.7 (t), 22.6 (q), 24.4 (q), 15.2 (q), 14.0 (q). IR (neat) ν (cm^{-1}) 3334 (b), 2953, 2919, 1455. HRMS calcd for $C_{17}H_{32}O(Na^+)$: 289.2502, found: 289.2506.

(2*S*)-(*E*)-4-(*p*-Menthan-3-yl)-1-phenylbut-3-en-2-ol (18d). Done according to the general procedure B. 17 mg (51%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35-7.10 (m, 5H), 5.83 (dt, 1H, *J* = 14.6, 6.8), 5.63 (dd, 1H, *J* = 15.3, 7.2), 4.42 (dd, 1H, *J* = 7.2, 4.1 Hz), 3.41 (d, 2H, *J* = 6.8 Hz), 2.05-1.83 (m, 2H), 1.80-2.50 (m, 4H), 1.45-1.20 (m, 2H), 1.10-0.60 (m, 8H), 0.91 (d, 3H, *J* = 6.5 Hz), 0.84 (d, 3H, *J* = 6.9 Hz), 0.78 (d, 3H, *J* = 7.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.4 (s), 131.7 (d), 130.1 (d), 128.6 (d), 128.5 (d), 126.2 (d), 72.3 (d), 44.7 (d), 44.3 (d), 39.1 (t), 35.4 (t), 34.2 (t), 32.7 (d), 26.3 (d), 24.4 (t), 23.0 (q), 21.6 (q), 15.3 (q). IR (neat) ν (cm^{-1}) 3361 (b), 2952, 2913, 1494, 1453. HRMS calcd for $C_{20}H_{30}O(Na^+)$: 309.2189, found: 309.2192.

(1*R*)-(*E*)-1-Cyclohexyl-3-(*p*-menthan-3-yl)prop-2-en-1-ol (18e). Done according to the general procedure B. 8 mg (40%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.80 (dd, 1H, *J* = 15.3, 9.6 Hz), 5.48 (dd, 1H, *J* = 15.3, 7.7 Hz), 3.78 (bt, 1H, *J* = 7.4 Hz), 2.58 (dd, 1H, *J* = 9.5, 4.0 Hz), 1.89-1.47 (m, 10H), 1.48-1.32 (m, 2H), 1.32-1.05 (m, 6H), 1.05-0.78 (m, 40.86 (d, 3H, *J* = 6.2 Hz)0.84 (d, 3H, *J* = 6.2 Hz), 0.82 (d, 3H, *J* = 6.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 133.6 (d), 132.0 (d), 78.2 (d), 47.1 (d), 43.8 (d), 42.8 (t), 40.0 (d), 35.7 (t), 30.3 (d), 28.9 (t), 28.6 (t), 26.8 (d), 26.6 (t), 26.2 (t), 26.1 (t), 25.6 (t), 22.9 (q), 21.2 (q), 20.6 (q). IR (neat) ν (cm^{-1}) 3299 (b), 2961, 1472, 1453. HRMS calcd for $C_{19}H_{34}O(Na^+)$: 301.2502, found: 301.2502.

(2*R*)-(*E*)-4-(*p*-Menthan-3-yl)but-3-en-1,2-diol (18f). Done according to the general procedure B. 14 mg (54%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 5.56 (dd, 1H, *J* = 15.5, 8.9 Hz), 5.41 (dd, 1H, *J* = 15.4, 6.4 Hz), 4.19 (m, 1H), 3.62 (dd, 1H, *J* = 11.2, 3.6 Hz), 3.47 (dd, 1H, *J* = 11.5, 7.6 Hz), 2.2-2.0 (bm, 2H), 2.0-1.5 (m, 6H), 1.45-1.29 (m, 1H), 1.07-0.75 (m, 4H), 0.87 (d, 3H, *J* = 6.8 Hz), 0.86 (d, 3H, *J* = 6.8 Hz), 0.70 (d, 3H, *J* = 6.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.3 (d), 127.5 (d), 73.4 (d), 66.8 (t), 47.2 (d), 44.5 (d), 43.2 (t), 35.2 (t), 32.5 (d), 28.3 (d), 24.2 (t), 22.7 (q), 21.6 (q), 15.5 (q). IR (neat) ν (cm^{-1}) 3340 (b), 2951, 2914, 1454. HRMS calcd for $C_{14}H_{26}O_2(Na^+)$: 249.1825, found: 249.1830.

(2*R*)-(*E*)-1-(*t*-Butyldimethylsilyloxy)-4-(*p*-menthan-3-yl)but-3-en-2-ol (18g). Done according to the general procedure B. 84 mg (68%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.53 (dd, 1H, *J* = 15.5, 8.9 Hz), 5.36 (dd, 1H, *J* = 15.5, 6.2 Hz), 4.10 (m, 1H), 3.60 (dd, 1H, *J* = 9.9, 3.8 Hz), 3.42 (dd, 1H, *J* = 9.9, 7.7 Hz), 2.49 (d, 1H, *J* = 3.1 Hz), 1.99-1.5 (m, 5H), 1.46-1.26 (m, 1H), 1.05-0.76 (m, 4H), 0.91 (s, 9H), 0.86 (d, 3H, *J* = 6.7 Hz), 0.85 (d, 3H, *J* = 6.7 Hz), 0.71

(d, 3H, *J* = 6.9 Hz), 0.08 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.4 (d), 127.3 (d), 72.8 (d), 67.3 (t), 47.1 (d), 44.3 (d), 43.2 (t), 35.2 (t), 32.4 (d), 28.0 (d), 25.9 (q), 24.1 (t), 22.6 (q), 21.5 (q), 18.3 (s), 15.4 (q), -5.3 (q), -5.4 (q). IR (neat) ν (cm^{-1}) 3419 (b), 2952, 2927, 1463. HRMS calcd for $C_{20}H_{40}O_2Si(Na^+)$: 363.2690, found: 363.2691.

(1*R*)-(*E*)-1-Trifluoromethyl-4-(*p*-menthan-3-yl)-prop-2-en-1-ol (18i). Done according to the general procedure B. 33 mg (66%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.78 (dd, 1H, *J* = 15.5, 9.3 Hz), 5.49 (dd, 1H, *J* = 15.5, 6.7 Hz), 4.39 (sextet, 1H, *J* = 6.9 Hz), 2.09-1.93 (m, 2H), 1.80-1.68 (m, 2H), 1.51-1.24 (m, 2H), 1.10-0.75 (m, 5H), 0.88 (d, 3H, *J* = 6.8 Hz), 0.87 (d, 3H, *J* = 6.8 Hz), 0.72 (d, 3H, *J* = 6.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.6 (d), 121.0 (d), [$\underline{C}F_3$ = 129.6, 126.2, 122.5, 118.7], [$\underline{C}H$-CF_3 = 72.3, 71.9, 71.4, 71.0], 47.0 (d), 44.5 (d), 42.5 (t), 35.0 (t), 32.3 (d), 28.2 (d), 24.0 (t), 22.5 (q), 21.4 (q), 15.3 (q). ^{19}F NMR (285 MHz, $CDCl_3$) δ -79.55 (d, 3F, *J* = 9 Hz). IR (neat) ν (cm^{-1}) 3379 (b), 2954, 1455. HRMS calcd for $C_{14}H_{23}OF_3(Na^+)$: 287.1593, found: 287.1587.

(5*R*)-5-Pentylfuran-2(5H)-one (20). Alcohol **17c** (200 mg, 751 µmol) was dissolved in dry DCM (15 mL) under nitrogen and the resulting solution was cooled to 0 °C. Et_3N (0.41 mL, 3.0 mmol) and acryloyl chloride (0.12 mL, 1.5 mmol) were added, after which the ice bath was removed. The reaction mixture was stirred at rt for 1.5 h. Water and DCM were added and the phases were separated. The aqueous phase was extracted 3 times with DCM and the organic phases were combined. The resulting organic phase was washed with water and then brine. The resulting organic phase was dried with anhydrous magnesium sulfate and filtered through sintered glass. The filtrate was concentrated under reduced pressure to yield the crude product as a slightly yellow oil (285 mg). The crude product was purified by flash chromatography on silica gel eluting with a mixture of hexanes and ethyl acetate (95:5) to yield the pure desired (6*R*)-(*E*)-8-(*p*-menthan-3-yl)oct-7-en-6-ol, acryloyl ester **30** as a colorless oil (187 mg, 78%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.38 (dd, *J* = 17.3, 1.6 Hz, 1H), 6.11 (dd, *J* = 17.3, 10.3 Hz, 1H), 5.79 (dd, *J* = 10.3, 1.6 Hz, 1H), 5.49 (dd, J = 15.1, 9.0 Hz, 1H), 5.43 – 5.19 (m, 2H), 1.99 – 1.47 (m, 7H), 1.29 (q, J = 5.7, 4.3 Hz, 6H), 1.05 – 0.93 (m, 2H), 0.86 (td, J = 6.5, 3.5 Hz, 11H), 0.69 (d, J = 6.9 Hz, 3H).

Ester **30** (40 mg, 0.13 mmol) was added to a oven-dried round-bottom two-neck flask equipped with a stir bar and a condenser under N_2 atmosphere. Dry toluene (11 mL) was added, and the remaining oxygen was removed by applying 3 freeze-thaw cycles. The solution was heated to reflux and a solution of 2nd generation Hoveyda-Grubbs catalyst (7.8 mg, 12 µmol) in dry toluene (1.2 mL) was added over 30 min. using a syringe pump. The reaction mixture was stirred under reflux for an additional 3 h. The reaction mixture was cooled to rt and DMSO (44 µL, 0.62 mmol) was added. The reaction mixture was stirred at rt for 16 h. Solvent was removed under reduced pressure to yield the crude product as a brown mixture of oil and solids (141 mg). The crude product was purified by flash chromatography eluting with a mixture of hexanes and ethyl acetate (8:2) to yield the pure desired product **20** as a colorless oil (12 mg, 63%). $[\alpha]_D^{25}$: –86.3 (*c*=1.59, $CHCl_3$) litt.: –84.05 (c=0.71, $CHCl_3$ at 81%ee)[19]. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 (dd, J = 5.9, 1.2 Hz, 1H), 6.10 (dd, J = 5.7, 2.0 Hz, 1H), 5.03 (m, 1H), 1.79 – 1.57 (m, 2H), 1.52 – 1.38 (m, 2H), 1.35 – 1.25 (m, 4H), 0.89 (t, *J* = 6.7 Hz, 3H). The spectral data was identical to the published data.[10]

(3*R*)-3-Hydroxypiperidin-2-one (22). Alcohol **17j** (50 mg, 179 mol) was solubilized in dry MeOH (1.8 mL) and the solution was cooled to -78 °C. A stream of ozone (4%) was bubbled into the solution until a blue color remained. A stream of nitrogen was then bubbled through the solution to remove excess ozone while allowing the solution to warm to rt. Then, DMS (26 µL, 358 µmol) was added and the reaction mixture was stirred for 2 h. The solution was then concentrated under reduced pressure to yield an oil. Amylene (7.6 mL) and *t*-BuOH (19 mL) were added to this crude product. A solution of $NaClO_2$ (149 mg, 1.65 mmol) and sodium phosphate monobasic monohydrate (170 mg, 1.24 mmol) in water (6.6 mL) was added and the reaction mixture was stirred at rt for 20 min. Then, 0.1 N HCl was added, and the layers were separated. The aqueous layer was extracted 3 times with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4, filtered,

and after removal of the solvent under reduced pressure, the crude product **21** was purified using silica gel column chromatography eluting with a mixture of DCM, MeOH and AcOH (80:20:1) to yield the desired product **21** as a colorless oil (24 mg, 86%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.0-4.9 (bm, 2H (OHs)), 4.31 (t, *J* = 5.3 Hz, 1H), 3.36 (t, *J* = 6.2 Hz, 2H), 1.97 (m, 1H), 1.89 – 1.66 (m, 3H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 178.74 (s), 69.95 (d), 51.21 (t), 31.36 (t), 24.64 (t). IR (neat) ν (cm^{-1}) 3600-2600 (bs), 2927, 2092 (s), 1715 (s), 1451, 1247. HRMS calcd for $C_5H_9N_3O_3(Na^+)$: 182.0536, found: 182.0534.

The azido acid **21** (24 mg, 151 mmol) was dissolved in dry DCM (1.5 mL). Then, 5 wt % Pd on carbon was added (11 mg), and the mixture was stirred under an atmosphere of hydrogen for 35 min. The suspension was filtered through celite and rinsed with DCM and EtOAc to remove menthyl carboxylic acid. The celite was then rinsed with methanol to elute the desired amine. The amine solution was concentrated under reduced pressure to yield the pure amine as a colorless solid (10 mg). DCM (6 mL) was added, followed by DCC (45 mg) and stirred at rt for 21 h. Solvent was removed under reduced pressure to yield the crude product. The crude product was purified by flash chromatography eluting with a mixture of DCM and MeOH (9:1) to yield the pure desired product **22** as a white solid (13 mg, 40%).$[\alpha]_D^{25}$: +5.8 (*c*=0.27, $CHCl_3$) litt.: +6 (c=0.4, $CHCl_3$)[30]. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.28 (s, 1H), 4.04 (dd, *J* = 10.8, 5.8 Hz, 1H), 3.78 (s, 1H), 3.34-3.28 (m, 2H), 2.29-2.21 (m, 1H), 2.06-1.63 (m, 3H). The spectral data was identical to published data.[13]

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Supplementary Material

Copies of NMRs for all new compounds, HPLC traces and X-ray data for compound **17i** (deposition number CCDC 2290613).

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