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Enantiospecific syntheses of oxacyclodecanes from carvone *via* mild Lewis acid mediated etherifcation

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An efficient enantiospecific syntheses of oxatri-/tetra-cyclodecanes have been accomplished starting from (*R*)-carvone. A mild Lewis acid ($BF_3{\cdot}OEt_2$) mediated intramolecular etherification is used as the key step. Structurally aesthetic tri- and tetracyclic ethers have been synthesized.

Keywords: (*R*)-Carvone, terpenes, cyclic ethers, Lewis acid, etherification

Monoterpenes (a 10-carbon containing compounds) are the simplest compounds of terpenes and can be obtained from combination of two isoprene molecules. They constitute acyclic, monocyclic, bicyclic and tricyclic structures. The chief source of them are plants, flowers, fruits, leaves and spices. Notably, monoterpenes are useful chiral auxiliaries, while their potential application has not been still properly explored[1]. Though carbohydrates have been widely employed as chiral synthons[2], monoterepenes are essential starting materials in the enantioselective synthesis natural as well as unnatural products due to their ubiquitous nature. Monoterpenes are significant, as they are available as commercial chemicals. Further, unlike amino acids and carbohydrates, monoterpenes are found in both enantiomeric forms with limited stereocenters that helps to reduce unnecessary chemical reactions to dispose undesired chiral center(s). Furthermore, monoterpenes can be easily restructured into cyclic as well as acyclic fragments that permits implantation to the required carbocyclic cores of desired products. Since monoterpenes are chiral natural products, they are enantiomerically pure in nature. Thus, making use of monoterpenes to accomplish enantioselective total synthesis of natural and unnatural products is essential in the field of organic synthesis.

Xanthone based natural products are the chemical constituents of genus *Garcinia* (Figure 1)[3]. Most of *Garcinia* natural xanthones and their derivatives[4] exhibit potent biological activities. These natural products in common possess oxatricyclo [4.3.1.$0^{3,7}$] decane part structure. To the best of our knowledge, very few reports exist on the synthesis of *Garcinia* xanthones[5]. only a few research groups have attempted the synthesis of oxatricyclo [4.3.1.$0^{3,7}$] decane core[6]. In continuation to our research interest on the accomplishment of enantiomerically pure terpene natural products[7] and chiron based approaches[8] using commercially available chiral monoterpene (*R*)-carvone, herein, we describe a synthetic strategy for the enantiospecific synthesis of oxatricyclo [4.3.1.$0^{3,7}$] decanes using mild Lewis acid ($BF_3{\cdot}OEt_2$) promoted intramolecular etherification, as the key step.

It was intended that the tri- and tetra-cyclic ethers **5** could be obtained from ketones **6** through a stereoselective reduction of carbonyl group and acid catalyzed intramolecular etherification sequence (Scheme I). We envisioned that the suitably positioned double bond of isopropenyl moiety could be served as an ideal non-disposable electrophilic functional group for intramolecular nucleophilic addition of hydroxyl group, in the presence of suitable acid as promoter. The required ketones **6** which in turn can be synthesized using the chiral starting material(s) (*R*)-carvone(s) **7**.

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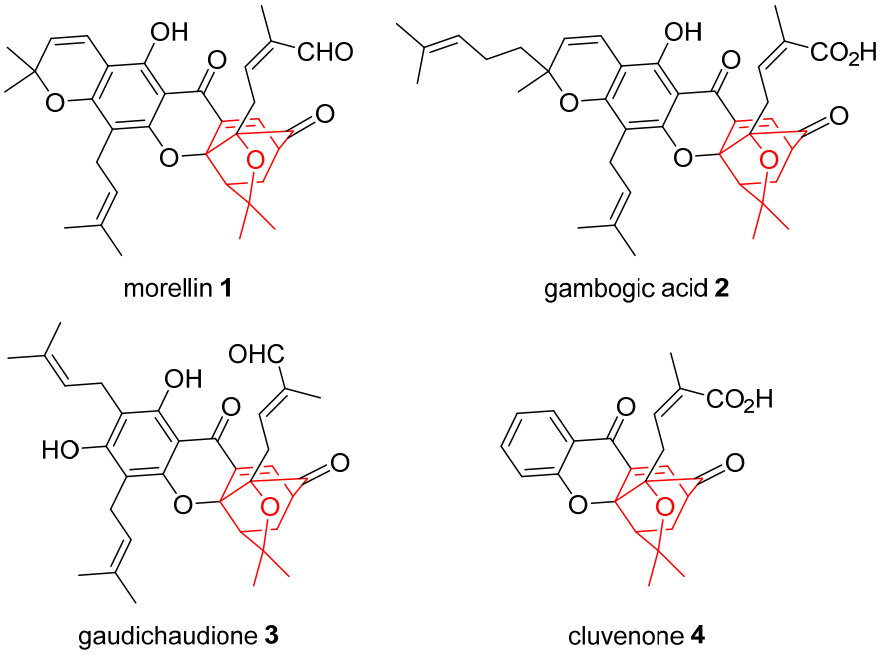
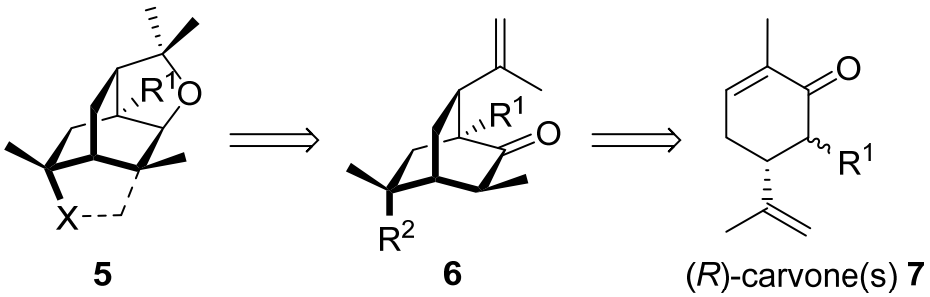


Figure 1



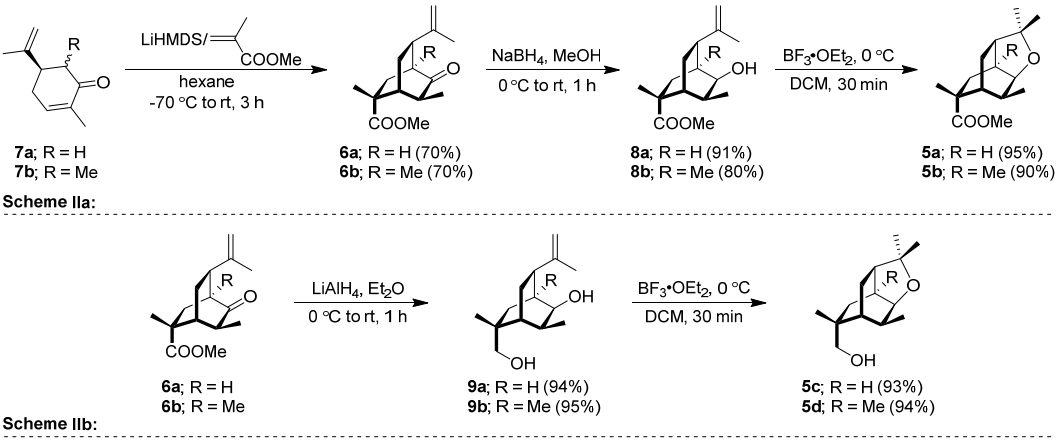
Scheme I — Retrosynthetic analysis of tri-/tetra-cyclic ethers **5**

To begin with, synthesis of enol ester **8a** was planned for this study[9,10], as depicted in Scheme IIa. Thus, generation of kinetic lithium enolate of (*R*)-carvone **7a** with lithium hexamethyldisilazide (LiHMDS) in hexane and *in situ* double Michael addition with the Michael acceptor methyl methacrylate, delivered the bicylic keto ester **6a** in 70% yield, with high stereoselectivity (Scheme IIa). Stereoselective reduction of carbonyl group of **6a** with $NaBH_4$, afforded the *exo*-secondary alcohol **8a**, in 91% yield. The stereoselective outcome of the reduction **6a** can be explained on the basis of approaching the reducing agent ($NaBH_4$) from the less hindered *exo*-face of the ketone. To our delight, the intramolecular etherification reaction of **8a** with 0.5 equiv of the Lewis acid ($BF_3{\cdot}OEt_2$), gave the expected tricyclic ether **5a**, in excellent yield (Scheme IIa). On the other hand, reduction of both keto as well as ester groups of **6a** with $LiAlH_4$, furnished the diol **9a** in 94% yield[11]. Thereafter, intramolecular etherification of the diol **9a** in the presence of $BF_3{\cdot}OEt_2$, afforded the tricyclic ether **5c** (Scheme IIb). Similarly, repetition of the above synthetic sequence with 6-methyl carvone **7b**[12,13], afforded the cyclic ethers **5b** and **5d**, in 90 and 94% yields, respectively (Scheme IIa and Scheme IIb).

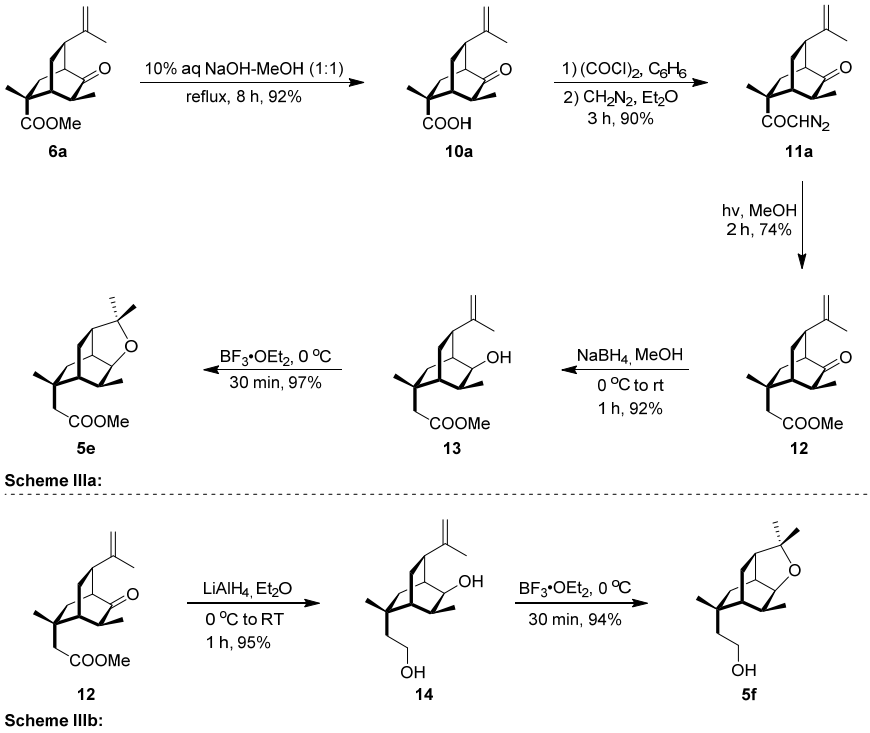
After successfully demonstrating the Lewis acid ($BF_3{\cdot}OEt_2$) mediated intramolecular etherification for the accomplishment of tri-cyclic ethers (**5a-d**, Scheme IIa and Scheme IIb), we turned our attention on the synthesis of cyclic ethers **5e** and **5f** (Scheme IIIa and Scheme IIIb). Thus, the bicyclic keto ester **6a** was transformed into the homologated ester **12** using base hydrolysis, acid chloride formation, diazotization and photochemically induced

one carbon homologation protocol. Then, selective reduction of the ketone of keto ester **12** with $NaBH_4$ and $BF_3{\cdot}OEt_2$ mediated etherification sequence, furnished the cyclic ether **5e** (Scheme IIIa). Reduction of both ketone and ester groups of **12** with $LiAlH_4$, afforded the diol **14**, which on catalytic $BF_3{\cdot}OEt_2$ reaction, gave the cyclic ether **5f** (Scheme IIIb).

Furthermore, to demonstrate the applicability of the strategy, next, we aimed at the synthesis of tetra-cyclic ethers. The bicyclic keto ester **6b** was chosen for this study. Thus, base hydrolysis of the bicyclic keto ester **6b**, gave the carboxylic acid **10b**. Reaction of carboxylic acid **10b**, with oxalyl chloride and subsequent diazotization, furnished the diazoketone **11b**. Thereafter, the C-H insertion reaction of rhodium carbenoid **11b** afforded the isotwistanedione **15**[9b]. Reduction of the diketone **15** with $LiAlH_4$, furnished the diol **16**, with high stereoselectivity. The stereoselectivity in the reduction of diketone **15** was predicted based on the reason that the reducing agent ($LiAlH_4$) would approach the ketones from the less hindered *exo*-faces of the compound and thus,



Scheme II — Synthesis of tri-cyclic ethers **5a-d** from (*R*)-carvones **7a-b**



Scheme III — Synthesis of tri-cyclic ethers **5e-f** from **6a**

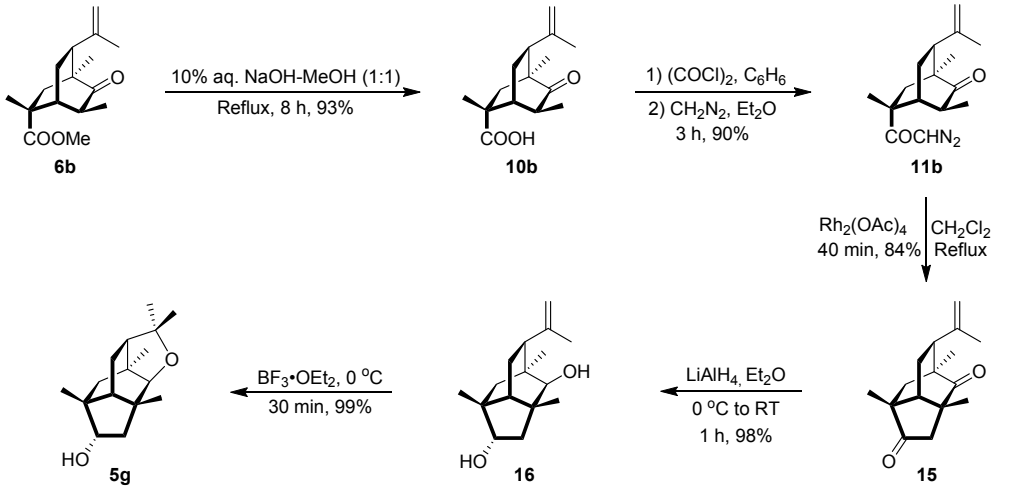
facilitate its hydride attack on the carbonyl groups from anti-position to the bulky moieties. Finally, $BF_3{\cdot}OEt_2$ mediated intramolecular cyclization, gave the tetracyclic ether **5g**, in near quantitative yield (Scheme IVa). Chemoselective mesylation of relatively less hindered hydroxyl group of the diol **16** led to the formation of **17**. Final etherification of **17**, gave the tetra-cyclic ether **5h** in near quantitative yield (Scheme IVb).

In summary, we have established enantiospecific syntheses of oxatri-/tetra-cyclodecanes from chiral monoterpene (*R*)-carvone. A mild Lewis acid ($BF_3{\cdot}OEt_2$) mediated intramolecular etherification was used as the key step. Structurally aesthetic tri- and tetracyclic ethers have been accomplished.

Experimental Section

Melting points were recorded on a Buchi M-560 apparatus and are uncorrected. IR spectra were recorded on a Jasco FTIR 410 spectrophotometer. ^1H (300 MHz) and ^{13}C (75 MHz) NMR spectra were recorded on JEOL JNM k-300 spectrometer using a 1:1 mixture of $CDCl_3$ and CCl_4 as the solvent. The chemical shifts (δ, ppm) and coupling constants (Hz) are reported in the standard fashion with reference to either internal tetramethylsilane (for ^1H) or the central line (77.0 ppm) of $CDCl_3$ (for ^{13}C). In the ^{13}C NMR, the nature of carbons (C, CH, CH_2 and CH_3) was determined by recording the DEPT-135 spectra, and is given in parentheses. High-resolution mass spectra were recorded using Micromass Q-TOF micro mass spectrometer using electron spray ionization (ESI) mode. Optical rotations were measured using a Jasco DIP-370 digital polarimeter and $[\alpha]_D$ values are given in units of 10^{-1} deg cm^2 g^{-1}. All small scale dry reactions were carried out using standard syringe-septum technique. Reactions were monitored by TLC on silica gel using a combination of hexane and ethyl acetate or hexane and methylene chloride as eluents. Acme's silica gel (100–200 mesh) was used for column chromatography (approximately 20 g per one gram of crude material).

(−)-Methyl(*1R,2R,4S,5S,6S,8S*)-5-hydroxy-8-isopropenyl-2,4,6-trimethyl-bicyclo[2.2.2]octane-2-carboxylate, 8b: To an ice cold, magnetically stirred solution of the keto ester **6b** (100 mg, 0.38 mmol) in dry methanol (2 mL) was added $NaBH_4$ (43 mg, 1.14 mmol) and stirred for 1 h at the same temperature. The solvent was removed under reduced pressure and water (3 mL) was added to the residue followed by 3



Scheme IV — Synthesis of tetracyclic ethers **5g-h** from **6b**

N aqueous HCl (3 mL) and extracted with CH_2Cl_2 (3 × 5 mL). The combined CH_2Cl_2 extract was washed with brine and dried (anhyd. Na_2SO_4). Evaporation of the solvent and purification of the residue on a silica gel column using ethyl acetate-hexane (1:30 to 1:10) as eluent furnished the secondary alcohol **8b** (81 mg, 80%) as oil. $[\alpha]_D^{27}$ **:** −106.5 (*c* 7.5, $CHCl_3$). IR (neat): 3568, 2950, 2929, 2875, 1728, 1629, 1456, 1375, 1274, 1211, 1134, 1105, 889 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$+CCl_4): δ 4.98 (2 H, s, CH_2=C), 3.66 (3 H, s, OCH_3), 3.44 (1 H, m, CH-OH), 2.30-2.00 (2 H, m), 2.00-1.60 (5 H, m), 1.86 (3 H, s, olefinic-CH_3), 1.60-1.10 (1 H, m), 1.30 (3 H, s) and 0.99 (3 H, s) [2 × *tert*-CH_3], 1.05 (3 H, d, *J* = 7.2 Hz, *sec*-CH_3); ^{13}C NMR (75 MHz, $CDCl_3$+CCl_4): δ 178.6 (C, O-C=O), 149.1 (C, *C*=CH_2), 113.9 (CH_2, CH_2=C), 75.9 (CH, CH-OH), 51.9 (CH_3, O-CH_3), 46.1 (C), 45.4 (2 C, CH, CH_2), 39.7 (CH), 39.0 (C), 34.6 (CH_3), 26.3 (CH_3), 25.4 (CH), 23.8 (CH_3), 21.5 (CH_2), 13.3 (CH_3); HRMS: *m/z* Calcd for $C_{16}H_{26}O_3Na$ (M+Na): 289.1780. Found: 289.1791.

(−)-(*1S,2S,3S,4R,5R,7R*)-5-Hydroxymethyl-7-isopropenyl-1,3,5-trimethyl-icyclo[2.2.2]octan-2-ol, 9b: To a cold (0 °C), magnetically stirred solution of the keto ester **6b** (100 mg, 0.38 mmol) in dry ether (3 mL) was added $LiAlH_4$ (43 mg, 1.14 mmol) and stirred for 1 h at RT. The reaction mixture was then diluted with ether (3 mL) and quenched with a few drops of water. The organic layer was separated and the aqueous phase was extracted with ether (3 × 4 mL). The combined organic layer was washed with brine and dried (anhyd. Na_2SO_4). Evaporation of the solvent and purification of the residue over a silica gel column using ethyl acetate-hexane (2:3) as eluent furnished the diol **9b** (86 mg, 95%) as oil. $[\alpha]_D^{27}$ **:** −72.3 (*c* 9.7, $CHCl_3$). IR (neat): 3429, 2922, 2875, 1631, 1454, 1375, 1024, 887 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$+CCl_4): δ 5.02 and 5.00 (2 H, 2 × s, CH_2=C), 3.45 and 3.23 (2 H, 2 × d, *J* = 10.5 Hz, CH_2OH), 3.38 (1 H, dd, *J* = 9.0 and 1.8 Hz, CH-OH), 2.50-1.60 (7 H, m), 1.87 (3 H, s, olefinic-CH_3), 1.40-0.70 (2 H, m), 1.13 (3 H, s) and 0.96 (3 H, s) [2 × *tert*-CH_3], 1.08 (3 H, d, *J* = 7.2 Hz, *sec*-CH_3); ^{13}C NMR (75 MHz, $CDCl_3$+CCl_4): δ 150.1 (C, *C*=CH_2), 113.5 (CH_2, *C*H_2=C), 76.8 (CH, CH-OH), 70.3 (CH_2, CH_2-OH), 47.6 (CH_2), 45.7 (CH), 38.9 (C), 37.4 (CH), 37.1 (C), 31.2 (CH), 25.9 (CH_3), 25.4 (CH_3), 24.1 (CH_3), 22.4 (CH_2), 13.5 (CH_3); HRMS: *m/z* Calcd for $C_{15}H_{26}O_2Na$ (M+Na): 261.1830. Found: 261.1828.

(−)-Methyl-2-[(*1R,2S,4S,6S,8R*)-8-isopropenyl-2, 6-dimethyl-5-oxobicyclo[2.2.2]oct-2-yl]-acetate, 12

Step 1: **Acid, 10a**: A magnetically stirred solution of the keto ester **6a** (1.0 g, 4 mmol) in methanol (5 mL) and 10% aqueous NaOH (5 mL) was refluxed for 8 h. The reaction mixture was cooled to RT and washed with CH_2Cl_2 (10 mL). Then, the aqueous layer was acidified with 3 *N* HCl and extracted with CH_2Cl_2 (3 × 10 mL). The CH_2Cl_2 extract was washed with brine and dried (anhyd. Na_2SO_4). Evaporation of the solvent furnished the acid **10a** (870 mg, 92%) as sticky solid, which was recrystallized from a mixture of hexane and CH_2Cl_2.

Step 2: **Acid chloride**: To a magnetically stirred solution of the acid **10a** (820 mg, 3.47 mmol) in dry benzene (3 mL) was added oxalyl chloride (6.95 mL, 0.61 mmol) and stirred for 2 h at RT. Evaporation of the solvent and excess oxalyl chloride under reduced pressure afforded the acid chloride, which was used immediately for the preparation of the diazoketone **11a**.

Step 3: **Diazoketone, 11a**: A solution of the acid chloride in dry ether (6 mL) was added drop wise to a cold (0 °C), magnetically stirred ethereal solution of diazomethane (excess, prepared from 2 g of *N*-nitroso-*N*-methylurea and 50 mL of 60% aqueous KOH solution and 50 mL of ether) and the reaction mixture was stirred at RT for 2 h. Careful evaporation of the excess diazomethane and solvent on water bath and rapid purification of the residue over a neutral alumina column using ethyl acetate-hexane (1:5) as eluent, furnished the diazoketone **11a** (831 mg, 90%) as yellow oil.

Step 4: **Homologated Ester, 12**: A solution of diazo ketone **11a** (800 mg, 3.07 mmol) in methanol (100 mL) was placed in a pyrex photochemical reactor and irradiated with a Hanovia medium pressure mercury vapor lamp for 2 h. Evaporation of the solvent and purification of the photolysate on a silica gel column using ethyl acetate-hexane (1:20) as eluent furnished the homologated ester **12** (600 mg, 74%) as oil. $[\alpha]_D^{25}$ **:** −53.8 (*c* 7.8, $CHCl_3$). IR (neat): 2951, 1734, 1720, 1644, 1450, 1377, 1198, 1105, 1016, 895 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$+CCl_4): δ 4.70 and 4.69 (2 H, 2 × s, CH_2=C), 3.65 (3 H, s,

OCH_3), 2.65-2.20 (5 H, m), 2.20-2.05 (1 H, m), 2.05-1.45 (4 H, m), 1.70 (3 H, s, olefinic-CH_3), 1.33 (3 H, s, *tert*-CH_3), 1.12 (3 H, d, J = 6.8 Hz, *sec*-CH_3); ^{13}C NMR (75 MHz, $CDCl_3$+CCl_4): δ 217.3 (C, C=O), 171.5 (C, O-C=O), 147.0 (C, *C*=CH_2), 110.3 (CH_2, *C*H_2=C), 51.2 (CH_3, OCH_3), 47.8 (CH), 45.7 (CH_2), 42.6 (2C, CH), 42.0 (CH), 38.9 (CH_2), 34.1 (C), 27.7 (CH_3), 23.4 (CH_2), 22.0 (CH_3), 13.0 (CH_3); HRMS: *m/z* Calcd for $C_{16}H_{24}O_3Na$ (M+Na): 287.1623. Found: 287.1622.

(−)-Methyl 2[(*1R,2S,4S,5S,6S,8R*)-5-hydroxy-8-isopropenyl-2,6-dimethyl-bicyclo[2.2.2]oct-2-yl]acetate, 13: To an ice cold, magnetically stirred solution of the keto ester **12** (80 mg, 0.3 mmol) in dry methanol (2 mL) was added $NaBH_4$ (34 mg, 0.9 mmol) and stirred for 1 h at the same temperature. The solvent was removed under reduced pressure and water (3 mL) was added to the residue followed by 3 *N* aqueous HCl (3 mL) and extracted with CH_2Cl_2 (3 × 5 mL). The combined CH_2Cl_2 extract was washed with brine and dried (anhyd. Na_2SO_4). Evaporation of the solvent and purification of the residue on a silica gel column using ethyl acetate-hexane (1:15 to 1:8) as eluent furnished the secodary alcohol **13** (74 mg, 92%) as oil. $[\alpha]_D^{25}$ **:**−131.0 (*c* 7.0, $CHCl_3$). IR (neat): 3570, 2929, 2873, 1736, 1635, 1450, 1379, 1323, 1248, 1198, 1163, 1109, 1066, 1016, 887 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$+CCl_4): δ 4.98 and 4.91 (2 H, s, CH_2=C), 3.78 (1 H, dt, J = 13.8 and 4.2 Hz, CH-OH), 3.64 (3 H, s, OCH_3), 2.37 and 2.50 (2 H, 2 × d, J = 13.8 Hz, CH_2-C=O), 2.40-2.10 (3 H, m), 1.96 (1 H, dd, J = 11.1, 9.3 and 1.8 Hz), 2.10-1.60 (3 H, m), 1.87 (3 H, s, olefinic-CH_3), 1.51 (1 H, dd, J = 13.8 and 4.2 Hz), 1.36 (1 H, dd, J = 13.8 and 1.8 Hz), 1.20 (3 H, s, *tert*-CH_3), 1.03 (3 H, d, J = 7.5 Hz, *sec*-CH_3); ^{13}C NMR (75 MHz, $CDCl_3$+CCl_4): δ 172.2 (C, O-C=O), 150.7 (C, C=CH_2), 109. 2 (CH_2, CH_2=C), 72.5 (CH, CH-OH), 51.1 (CH_3, OCH_3), 46.1 (CH_2), 41.0 (CH), 40.6 (CH_2), 38.6 (CH), 35.8 (CH), 34.3 (C), 31.5 (CH), 27.2 (CH_3), 23.0 (CH_3), 20.1 (CH_2), 13.1 (CH_3); HRMS: *m/z* Calcd for $C_{16}H_{26}O_3Na$ (M+Na): 289.1780. Found: 289.1773.

(−)-(*1S,2S,3S,4R,5S,7R*)-5-(2-Hydroxyethyl)-7-isopropenyl-3,5-dimethyl-bicyclo[2.2.2]-octan-2-ol, 14: To a cold (0 °C), magnetically stirred solution of the keto ester **12** (100 mg, 0.38 mmol) in dry ether (3 mL) was added $LiAlH_4$ (43 mg, 1.14 mmol) and stirred for 1 h at RT. The reaction mixture was then diluted with ether (5 mL) and quenched with a few drops of water. The organic layer was separated and the aqueous phase was extracted with ether (3 × 4 mL). The combined organic layer was washed with brine and dried (anhyd. Na_2SO_4). Evaporation of the solvent and purification of the residue over a silica gel column using ethyl acetate-hexane (2:3) as eluent furnished the diol **14** (86 mg, 95%) as oil. $[\alpha]_D^{25}$ **:** −156.5 (*c* 7.2, $CHCl_3$). IR (neat): 3377, 2925, 2879, 1452, 1377, 1107, 1018, 887 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$+CCl_4): δ 4.99 and 4.90 (2 H, 2 × s, CH_2=C), 3.77 (1 H, dd, J = 9.3 and 3.3 Hz, C*H*-OH), 3.75-3.40 (2 H, m, CH_2-OH), 2.40-1.60 (8 H, m), 1.86 (3 H, s, olefinic-CH_3), 1.61 (2 H, t, J = 7.5 Hz), 1.41 (1 H, dd, J = 13.8 and 4.2 Hz), 1.35-1.20 (1 H, m), 1.09 (3 H, s, *tert*-CH_3), 1.01 (3 H, d, J = 7.2 Hz, *sec*-CH_3); ^{13}C NMR (75 MHz, $CDCl_3$+CCl_4): δ 150.8 (C, *C*=CH_2), 109.1 (CH_2, *C*H_2=C), 72.6 (CH, CH-OH), 59.2 (CH_2, CH_2-OH), 45.1 (CH_2), 41.7 (CH_2), 40.8 (CH), 38.8 (CH), 35.9 (CH), 33.2 (C), 31.0 (CH), 27.2 (CH_3), 23.0 (CH_3), 19.9 (CH_2), 13.2 (CH_3); HRMS: *m/z* Calcd for $C_{15}H_{26}O_2Na$ (M+Na): 261.1830. Found: 261.1825.

(−)-(*1S,2R,3R,5S,6R,7S,9R*)-9-Isopropenyl-1,3,6-trimethyltricyclo[4.3.1.0^{3,7}]decane-2,5-diol, 16: To a cold (0 °C), magnetically stirred solution of the dione **15** (200 mg, 0.81 mmol) in dry ether (3 mL) was added $LiAlH_4$ (93 mg, 2.44 mmol) and stirred for 1 h at RT. The reaction mixture was then diluted with ether (5 mL) and quenched with a few drops of water. The organic layer was separated and the aqueous phase was extracted with ether (3 × 4 mL). The combined organic layer was washed with brine and dried (anhyd. Na_2SO_4). Evaporation of the solvent and purification of the residue over a silica gel column using ethyl acetate-hexane (2:3) as eluent furnished the diol **16** (199 mg, 98%) as colorless solid, which was recrystallized from a mixture of methanol and hexane. M.p.: 58-60 °C. $[\alpha]_D^{25}$**:** −113.9 (*c* 4.6, $CHCl_3$). IR (neat): 3421, 3070, 2947, 2869, 1631, 1452, 1375, 1074, 1045, 1016, 887, 739 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$+CCl_4): δ 5.03 (2 H, s, CH_2=C), 3.61 (1 H, dd, J = 9.9 and 6.6 Hz, CH-OH), 3.08 (1 H, d, J = 5.4 Hz), 2.02-1.90 (4 H, m), 2.00-1.60 (2 H, m), 1.86 (3 H, s, olefinic-CH_3), 1.62 and 0.77 (2 H, 2 × d, J = 14.4 Hz), 1.30-0.90 (2 H, m), 1.07 (3 H, s), 1.04 (3 H, s) and 1.03 (3 H, s) [3 × *tert*-CH_3]; ^{13}C NMR (75 MHz, $CDCl_3$+CCl_4): δ 150.0 (C, C=CH_2), 113.5 (CH_2, CH_2=C), 87.7 (CH, CH-OH), 78.5 (CH, CH-OH), 49.8 (CH_2), 47.0 (CH), 46.8 (CH), 43.5 (C),

43.0 (C), 42.6 (CH_2), 37.5 (C), 26.1 (CH_3), 24.4 (CH_3), 24.1 (CH_3), 21.8 (CH_2), 20.8 (CH_3); HRMS: *m/z* Calcd for $C_{16}H_{26}O_2Na$ (M+Na): 273.1830. Found: 273.1842.

(−)-(*1S,2R,3R,5S,6R,7S,9R*)-2-Hydroxy-9-isopropenyl-1,3,6-trimethyltricyclo[4.3.1.0^{3,7}]decan- 5-yl-methanesulfonate, 17: To a cold (0 °C), magnetically stirred solution of the diol **16** (100 mg, 0.4 mmol) in pyridine (1 mL) and CH_2Cl_2 (1 mL) was added methanesulfonyl chloride (0.15 mL, 1.9 mmol) and the reaction mixture was stirred for 1 h at RT. It was then diluted with water (2 mL) and extracted with CH_2Cl_2 (3 × 3 mL). The organic layer was washed with 3 *N* aqueous HCl, saturated aqueous $NaHCO_3$ solution and brine, and dried (anhyd. Na_2SO_4). Evaporation of the solvent and purification of the residue over a silica gel column using ethyl acetate-hexane (2:3) as eluent furnished the mesylate **17** (128 mg, 98%) as colorless solid, which was recrystallized from a mixture of methanol and hexane. M.p.: 88-90 °C. $[\alpha]_D^{25}$**:** −65.6 (*c* 8.8, $CHCl_3$). IR (neat): 3565, 2949, 2873, 1633, 1455, 1350, 1176, 1075, 956, 924, 877, 810 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$+CCl_4): δ 4.96 and 4.94 (2 H, 2 × s, CH_2=C), 4.37 (1 H, dd, *J* = 9.6 and 6.3 Hz, C*H*-OMs), 3.07 (1 H, s), 2.92 (3 H, s, OMs), 2.80 (1 H, dd, *J* = 14.7 and 9.9 Hz), 2.10-1.60 (5 H, m), 1.79 (3 H, s, olefinic-CH_3), 1.53 and 0.85 (2 H, 2 × d, *J* = 14.1 Hz), 1.47 (1 H, dd, *J* = 14.7 and 6.3 Hz), 1.08 (3 H, s), 1.04 (3 H, s) and 0.96 (3 H, s) [3 × *tert*-CH_3]; ^{13}C NMR (75 MHz, $CDCl_3$+CCl_4): δ 149.1 (C, C=CH_2), 114.0 (CH_2, CH_2=C), 87.1 (CH, CH-OMs), 87.0 (CH, CH-OH), 47.3 (CH_2), 46.5 (CH), 45.7 (CH), 43.5 (C), 43.3 (2C, C, CH_2), 38.1 (CH_3), 37.4 (C), 25.7 (CH_3), 24.0 (CH_3), 23.8 (CH_3), 21.4 (CH_2), 20.5 (CH_3); HRMS: *m/z* Calcd for $C_{16}H_{24}O_1Na$ [(M+Na)-(MsOH)]: 255.1725. Found: 255.1740.

General procedure for intramolecular etherification reaction (GP)

To a cold (0 °C), magnetically stirred solution of the alcohol **8/9/13/14/16/17** (0.2 mmol) in dry CH_2Cl_2 (3 mL) was added a catalytic amount of $BF_3{\cdot}OEt_2$ (0.1 mmol) and stirred for 30 min at the same temperature. Saturated aq. $NaHCO_3$ was added to the reaction mixture and the organic layer was extracted with CH_2Cl_2 (3 × 3 mL). It was then washed with brine, and dried (anhyd. Na_2SO_4). Evaporation of the solvent and purification of the residue over a silica gel column using ethyl acetate-hexane as eluent furnished the ether **5** as oil/solid.

(−)-Methyl-(*1R,2S,3S,6R,7S,9R*)-2,5,5,9-tetramethyl-4-oxatricyclo[4.3.1.0^{3,7}]decane-9-carboxylate, 5a: GP was followed with alcohol **8a** (50 mg, 0.2 mmol), CH_2Cl_2 (3 mL) and $BF_3{\cdot}OEt_2$ (0.012 mL, 0.1 mmol). Purification of the residue over a silica gel column using ethyl acetate-hexane (1:20) as eluent furnished the ether **5a** (47 mg, 95%) as oil. $[\alpha]_D^{27}$**:** −73.3 (*c* 4.5, $CHCl_3$). IR (neat): 2925, 1732, 1456, 1375, 1265, 1221, 1117, 1063, 985, 964, 858, 814, 769 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$+CCl_4): δ 3.82 (1 H, t, *J* = 11.7 Hz, CH-O), 3.59 (3 H, s, OCH_3), 2.60-2.30 (2 H, m), 1.80-1.50 (4 H, m), 1.50-1.20 (2 H, m), 1.21 (3 H, s), 1.17 (3 H, s) and 1.14 (3 H, s) [3 × *tert*-CH_3], 0.83 (3 H, d, *J* = 7.2 Hz, *sec*-CH_3); ^{13}C NMR (75 MHz, $CDCl_3$+CCl_4): δ 178.6 (C, O-C=O), 81.1 (C, C-O), 77.4 (CH, CH-O), 51.8 (CH_3, OCH_3), 44.1 (C), 41.2 (CH), 37.3 (CH), 36.7 (2C, CH), 29.7 (CH_2), 27.9 (CH_2), 26.2 (CH_3), 24.1 (CH_3), 17.9 (CH_2), 13.9 (CH_3); HRMS: *m/z* Calcd for $C_{15}H_{24}O_3Na$ (M+Na): 275.1623. Found: 275.1631.

(−)-Methyl-(*1R,2S,3S,6R,7S,9R*)-2,5,5,7,9-pentamethyl-4-oxatricyclo[4.3.1.0^{3,7}]decane-9-carboxylate, 5b: GP was followed with alcohol **8b** (70 mg, 0.26 mmol), CH_2Cl_2 (3 mL), and $BF_3{\cdot}OEt_2$ (0.02 mL, 0.13 mmol). Purification of the residue over a silica gel column using ethyl acetate-hexane (1:10) as eluent furnished the ether **5b** (63 mg, 90%) as oil. $[\alpha]_D^{26}$**:** −39.2 (*c* 5.0, $CHCl_3$). IR (neat): 2964, 2930, 2925, 1732, 1456, 1377, 1250, 1199, 1138, 1103, 982, 854 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$+CCl_4): δ 3.62 (3 H, s, OCH_3), 3.53 (1 H, d, *J* = 6.6 Hz, CH-O), 2.60-2.30 (2 H, m), 2.00-1.70 (2 H, m), 1.65-1.00 (3 H, m), 1.35 (3 H, s), 1.27 (3 H, s), 1.20 (3 H, s) and 1.18 (3 H, s) [4 × *tert*-CH_3], 0.91 (3 H, d, *J* = 6.9 Hz, *sec*-CH_3); ^{13}C NMR (75 MHz, $CDCl_3$+CCl_4): δ 178.8 (C, O-C=O), 83.5 (CH, CH-O), 81.6 (C, C-O), 51.8 (CH_3, OCH_3), 47.8 (CH), 46.0 (C), 43.0 (C), 38.2 (CH_2), 38.0 (CH), 37.3 (CH), 30.7 (CH_3), 28.3 (CH_3), 28.0 (CH_3), 26.3 (CH_3), 20.1 (CH_2), 15.0 (CH_3); HRMS: *m/z* Calcd for $C_{16}H_{26}O_3Na$ (M+Na): 289.1780. Found: 289.1787.

(−)-(*1R,2S,3S,6R,7S,9R*)-(2,5,5,9-Tetramethyl-4-oxatricyclo[4.3.1.0^{3,7}]dec-9-yl)-methanol, 5c: GP was followed with the diol **9a** (50 mg, 0.22 mmol), CH_2Cl_2 (3 mL) and $BF_3{\cdot}OEt_2$ (0.014 mL, 0.11 mmol). Purification of the residue over a silica gel column using ethyl acetate-hexane (1:3) as eluent furnished the ether **5c** (46 mg, 93%) as oil. $[\alpha]_D^{26}$**:** −88.0 (*c* 4.5, $CHCl_3$). IR (neat): 3427, 2925, 2871, 1454, 1261,

1124, 1037, 983, 881, 810 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$+CCl_4): δ 3.80 (1 H, t, *J* = 6.0 Hz, CH-O), 3.40 and 3.20 (2 H, 2 × d, *J* = 10.8 Hz), 3.22 (1 H, br s, OH), 2.42 (1 H, s), 2.60-2.00 (1 H, m), 1.84 (1 H, quintet, *J* = 6.6 Hz), 1.90-1.40 (5 H, m), 1.24 (3 H, s), 1.17 (3 H, s) and 1.03 (3 H, s) [3 × *tert*-CH_3], 0.87 (3 H, d, *J* = 6.6 Hz, *sec*-CH_3); ^{13}C NMR (75 MHz, $CDCl_3$+CCl_4): δ 81.5 (C, C-O), 78.3 (CH, CH-O), 69.9 (CH_2, CH_2-OH), 41.5 (CH), 36.6 (CH), 35.2 (CH), 34.6 (C), 32.8 (CH), 29.7 (CH_3), 29.4 (CH_2), 25.6 (CH_3), 24.2 (CH_3), 18.8 (CH_2), 13.8 (CH_3); HRMS: *m/z* Calcd for $C_{14}H_{24}O_2Na$ (M+Na): 247.1674. Found: 247.1675.

(−)-(*1R,2S,3S,6R,7S,9R*)-(2,5,5,7,9-Pentamethyl-4-oxatricyclo[4.3.1.0^{3,7}]dec-9-yl)-methanol, 5d: GP was followed with the diol **9b** (70 mg, 0.29 mmol), CH_2Cl_2 (3 mL) was added a catalytic amount of $BF_3{\cdot}OEt_2$ (0.02 mL, 0.15 mmol). Purification of the residue over a silica gel column using ethyl acetate-hexane (1:3) as eluent furnished the ether **5d** (66 mg, 94%) as colorless solid, which was recrystallized from a mixture of methanol and hexane. M.p.: 58-60 °C. $[\alpha]_D^{26}$**:** −61.0 (*c* 4.8, $CHCl_3$). IR (neat): 3421, 2954, 2923, 2875, 1458, 1377, 1024, 974, 867 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$+CCl_4): δ 3.49 and 3.19 (2 H, 2 × d, *J* = 7.5 Hz, CH_2-OH), 3.45 (1 H, d, *J* = 12.0 Hz, CH-O), 2.21 (1 H, br s, OH), 2.20-1.95 (1 H, m), 2.00-1.70 (2 H, m), 1.70-1.50 (1 H, m), 1.50-0.98 (3 H, m), 1.36 (3 H, s), 1.29 (3 H, s), 1.13 (3 H, s) and 1.04 (3 H, s) [4 × *tert*-CH_3], 0.92 (3 H, d, *J* = 7.2 Hz, *sec*-CH_3); ^{13}C NMR (75 MHz, $CDCl_3$+CCl_4): δ 84.4 (CH, CH-O), 82.1 (C, C-O), 70.3 (CH_2, CH_2-OH), 47.9 (CH), 42.9 (C), 40.7 (CH_2), 35.9 (C), 35.3 (CH), 33.2 (CH), 30.7 (CH_3), 28.6 (CH_3), 28.4 (CH_3), 25.9 (CH_3), 20.8 (CH_2), 14.8 (CH_3); HRMS: *m/z* Calcd for $C_{15}H_{26}O_2Na$ (M+Na): 261.1830. Found: 261.1842.

(−)-Methyl-2[(*1R,2S,3S,6R,7S,9S*)-2,5,5,9-tetramethyl -4-oxatricyclo[4.3.1.0^{3,7}]dec-9-yl]-acetate, 5e: GP was followed with the secondary alcohol **13** (60 mg, 0.22 mmol), CH_2Cl_2 (3 mL) and $BF_3{\cdot}OEt_2$ (0.014 mL, 0.11 mmol). Purification of the residue over a silica gel column using ethyl acetate-hexane (1:10) as eluent furnished the ether **5e** (58 mg, 97%) as oil. $[\alpha]_D^{24}$**:** −89.1 (*c* 5.8, $CHCl_3$). IR (neat): 2952, 2925, 1737, 1454, 1379, 1192, 1142, 1012, 985, 814 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$+CCl_4): δ 3.89 (1 H, t, *J* = 6.0 Hz, CH-O), 3.63 (3 H, s, OCH_3), 2.46 (1 H, sextet, *J* = 3.0 Hz), 2.33 and 2.26 (2 H, 2 × d, *J* = 13.8 Hz, CH_2-C=O), 1.90 (1 H, quintet, *J*, 6.9 Hz), 1.85-1.60 (3 H, m), 1.52 (2 H, d, *J* = 3.0 Hz), 1.28 (3 H, s), 1.21 (3 H, s) and 1.12 (3 H, s) [3 × *tert*-CH_3], 1.00 (1 H, br s), 0.92 (3 H, d, *J* = 7.2 Hz, *sec*-CH_3); ^{13}C NMR (75 MHz, $CDCl_3$+CCl_4): δ 172.3 (C, O-C=O), 81.5 (C, C-O), 78.3 (CH, CH-O), 51.0 (CH_3, OCH_3), 45.6 (CH_2), 40.6 (CH), 38.8 (CH), 36.8 (CH), 33.5 (CH), 33.0 (C), 32.9 (CH_2), 29.6 (CH_3), 27.4 (CH_3), 24.2 (CH_3), 18.9 (CH_2), 13.8 (CH_3); HRMS: *m/z* Calcd for $C_{16}H_{26}O_3Na$ (M+Na): 289.1780. Found: 289.1784.

(−)-2[(*1R,2S,3S,6R,7S,9S*)-2,5,5,9-Tetramethyl-4-oxatricyclo[4.3.1.0^{3,7}]dec-9-yl]ethanol, 5f: GP was followed with the secondary alcohol **14** (70 mg, 0.29 mmol), CH_2Cl_2 (3 mL) and $BF_3{\cdot}OEt_2$ (0.019 mL, 0.15 mmol). Purification of the residue over a silica gel column using ethyl acetate-hexane (1:10) as eluent furnished the ether **5f** (66 mg, 94%) as oil. $[\alpha]_D^{24}$**:** −89.4 (*c* 6.4, $CHCl_3$). IR (neat): 3396, 2925, 1454, 1373, 1261, 1126, 1051, 985, 962, 885, 812 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$+CCl_4): δ 3.89 (1 H, t, *J* = 3.0 Hz, CH-O), 3.62 (2 H, s, CH_2-OH), 3.20 (1 H, br s, OH), 2.44 (1 H, br s), 1.97 (1 H, quintet, *J* = 6.9 Hz), 1.90-1.35 (8 H, m), 1.28 (3 H, s), 1.21 (3 H, s) and 1.02 (3 H, s) [3 × *tert*-CH_3], 0.92 (3 H, d, *J* = 6.9 Hz, *sec*-CH_3); ^{13}C NMR (75 MHz, $CDCl_3$+CCl_4): δ 81.7 (C, C-O), 78.4 (CH, CH-O), 59.3 (CH_2, CH_2-OH), 44.5 (CH_2), 41.0 (CH), 38.5 (CH), 36.9 (CH), 34.0 (CH_2), 32.9 (CH), 31.7 (C), 29.6 (CH_3), 27.4 (CH_3), 24.1 (CH_3), 18.9 (CH_2), 13.9 (CH_3); HRMS: *m/z* Calcd for $C_{15}H_{26}O_2Na$ (M+Na): 261.1830. Found: 261.1836.

(+)-(*1R,3S,4R,7R,9S,10R,12S*)-12-Hydroxy-1,3,6,6,10-pentamethyl-5-oxatetracyclo-[7.3.0.0^{3,7}.0^{4,10}.0^{1,9}] dodecane, 5g: GP was followed with the diol **16** (50 mg, 0.2 mmol), CH_2Cl_2 (3 mL) and $BF_3{\cdot}OEt_2$ (0.013 mL, 0.1 mmol). Purification of the residue over a silica gel column using ethyl acetate-hexane (1:4) as eluent first furnished the ether **5g** (49 mg, 99%) as colorless solid, which was recrystallized from a mixture of methanol and hexane. M.p.: 57-59 °C. $[\alpha]_D^{26}$**:** +8.57 (*c* 2.8, $CHCl_3$). IR (neat): 3421, 2925, 1452, 1377, 1252, 1128, 1043, 1020, 899 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$+CCl_4): δ 3.61 (1 H, dd, *J* = 9.3 and 8.1 Hz, CH-OH), 3.18 (1 H, s, CH-O), 1.97 (1 H, dd, *J* = 13.8 and 9.9 Hz), 1.85 (1 H, dd, *J* = 13.8 and 5.1 Hz), 1.80-1.55 (5 H, m), 1.38 (3 H, s), 1.30 (3 H, s), 1.26 (3 H, s), 1.03 (3 H, s) and 0.95 (3 H, s) [5 × *tert*-CH_3], 1.16 (1 H, d, *J* = 15.3 Hz), 0.88 (1 H, d, *J* = 5.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$+CCl_4): δ 93.0 (CH,

CH-O), 81.7 (C, C-O), 77.5 (CH, CH-OH), 50.1 (CH), 47.1 (CH_2), 45.0 (C), 44.6 (C), 44.3 (CH), 42.2 (C), 35.1 (CH_2), 30.8 (CH_3), 28.6 (CH_3), 28.4 (CH_3), 23.6 (CH_3), 23.5 (CH_3), 20.5 (CH_2); HRMS: *m/z* Calcd for $C_{16}H_{26}O_2Na$ (M+Na): 273.1830. Found: 273.1848.

(+)-(*1R,3S,4S,7R,9S,10R,12S*)-1,3,6,6,10-Pentamethyl -5-oxatetracyclo[7.3.0^{3,7}.0^{4,10}.0^{1,9}]dodecan- 12-yl-methanesulfonate, 5h: GP was followed with the mesylate **17** (90 mg, 0.27 mmol), CH_2Cl_2 (3 mL) and $BF_3{\cdot}OEt_2$ (0.02 mL, 0.14 mmol). Purification of the residue over a silica gel column using ethyl acetate-hexane (1:4) as eluent furnished the ether **5h** (89 mg, 99%) as colorless solid, which was recrystallized from a mixture of methanol and hexane. M.p.: 112-114 °C. $[\alpha]_D^{26}$ **:** +5.8 (*c* 10.4, $CHCl_3$). IR (neat): 2950, 2925, 2871, 1452, 1377, 1356, 1253, 1176, 1130, 1051, 1034, 962, 945, 928, 901, 887, 868, 835, 827 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$+CCl_4): δ 4.42 (1 H, dd, *J* = 9.9 and 4.8 Hz, CH-OMs), 3.20 (1 H, s, CH-O), 2.96 (3 H, s, OMs), 2.14 (1 H, dd, *J* = 14.4 and 9.9 Hz), 1.87 (1 H, dd, *J* = 14.7 and 5.7 Hz), 1.80-1.55 (1 H, m), 1.63 and 1.60 (2 H, 2 × d, *J* = 7.5 Hz), 1.46 (1 H, dd, *J* = 14.7 and 7.5 Hz), 1.36 (3 H, s), 1.28 (3 H, s), 1.25 (3 H, s), 1.04 (3 H, s) and 1.03 (3 H, s) [5 × *tert*-CH_3], 1.35-1.20 (1 H, m), 0.94 (1 H, d, *J* = 15.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$+CCl_4): δ 92.5 (CH, CH-O), 86.0 (CH, CH-OMs), 81.8 (C, C-O), 49.6 (CH), 45.4 (C), 44.4 (C), 44.3 (CH_2), 43.0 (CH), 42.0 (C), 38.2 (CH_3, OMs), 35.8 (CH_2), 30.7 (CH_3), 28.4 (CH_3), 28.0 (CH_3), 23.3 (CH_3), 23.1 (CH_3), 20.2 (CH_2); HRMS: *m/z* Calcd for $C_{16}H_{25}O_1$ [(M+H)-(MsOH)]: 233.1905. Found: 1913.

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