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Preparation and application of (+)-(3,3-dimethyl-2-methylenenorbornan-1-yl)methyl methanesulfonate: a new and versatile chiral fenchone analogue☆

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Abstract—The preparation of (+)-(3,3-dimethyl-2-methylenenorbornan-1-yl)methyl methanesulfonate (**9**) was carried out in 2 steps, dihydroxylation and mesylation, from (−)-2-methylenebornane. Hydrolysis and reduction of **9** gave a fenchyl alcohol (**2**) and a methylenefenchone (**21**), respectively. Oxidation of **9** afforded a new analogue (**23**) of the class of oxatricyclo compounds. Treatment of **9** with NBS resulted in a Wagner–Meerwein rearrangement to produce brominated methylenebornane derivatives (**25** and **26**), which are also new compounds.
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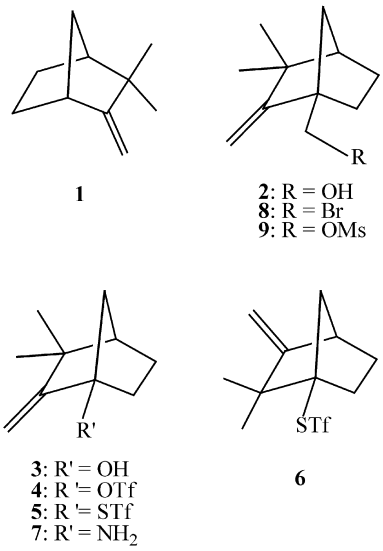
1. Introduction

Alkenes with fenchone-type skeleton have shown to be useful starting materials or intermediates for the synthesis of highly valuable compounds such as chiral auxiliaries and natural products. For example, Malpass and Tweddle[1] had converted parent camphene (**1**, Fig. 1) into camphene lactones and lactams via Wagner–Meerwein rearrangement. On the other hand, fenchyl alcohol **2**, originally prepared from camphor through several steps,[2] was employed as the precursor for the synthesis of epizizanoic acid.[3] Very recently, Garcia Martinez et al. have straightforwardly synthesized C10-bromo,[4,5] C10-hydroxy,[6] C10-C-,[7] C10-S- and C10-Se-substituted[8] camphors, using 2-methylenenorbornan-1-ol[9] (**3**) as the chiral source. It is well known that alcohol **3** can be smoothly obtained in 3 synthetic steps,[5] also starting from camphor. Moreover, the enantiomer of norbornyl triflate **4**,[10] which is the key intermediate for the preparation of **3** and **7**,[11] reacts with *m*-CPBA to form spiro-oxiramic triflates.[12] In addition, norbornyl thiotriflate **5** had been found to quantitatively isomerize to thiotriflate **6**[13] in the presence of TfOH. Individual reductions of **5** and **6** by $LiAlH_4$ produced corresponding bridgehead thiols, which are useful precursors for the syntheses of other sulfur-containing compounds. Remarkably, brominated methylenefenchone[14] (**8**) can be also reduced to parent methylenefenchone without isomerization. So far, it seems that each of these methylenefenchone analogues (**1**–**8**) is a good precursor or intermediate for the preparation of single specific compound.

Thus, we are interested in obtaining a unique fenchyl alkene, which can be a versatile intermediate for the syntheses of various novel compounds. Herein, we wish to report on the preparation and reactions of **9**, which was obtained efficiently, furnishing norbornane analogues in high yields and stereoselectivities.



1

2: R = OH
8: R = Br
9: R = OMs

3: R' = OH
4: R '= OTf
5: R '= STf
7: R' = NH_2

6

Figure 1. Some alkenes with fenchone-type skeleton.

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Keywords: methylenenorbornane; fenchone analogue.

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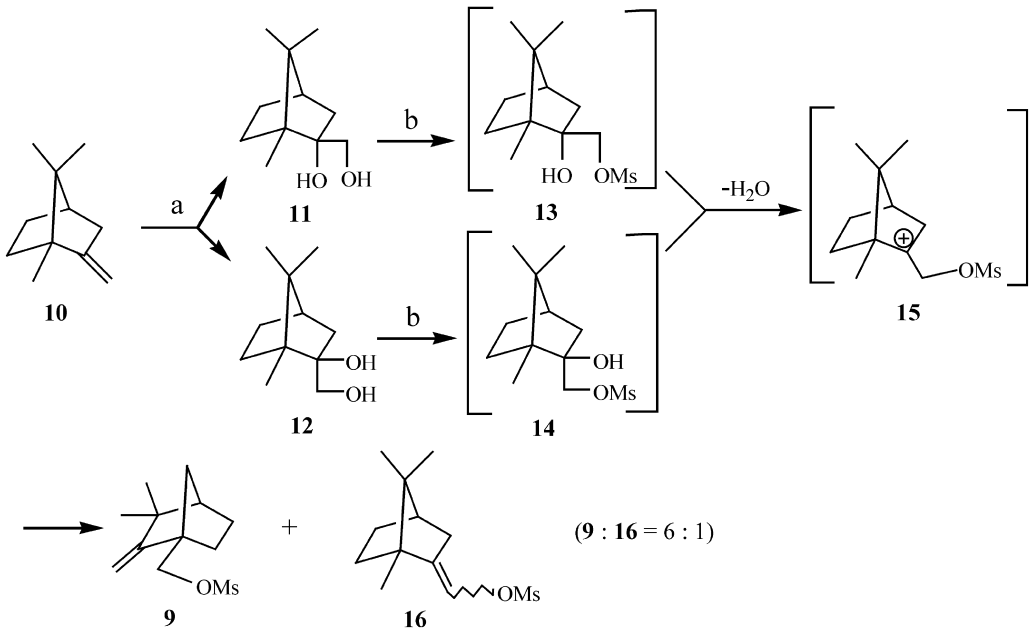
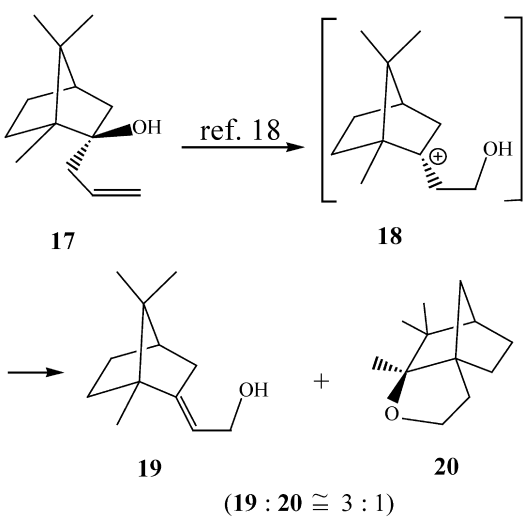


Scheme 1. (a) TMO, OsO_4, Py, *t*-BuOH, H_2O; (b) MsCl, Et_3N, CH_2Cl_2, 0°C to rt.

2. Results and discussions

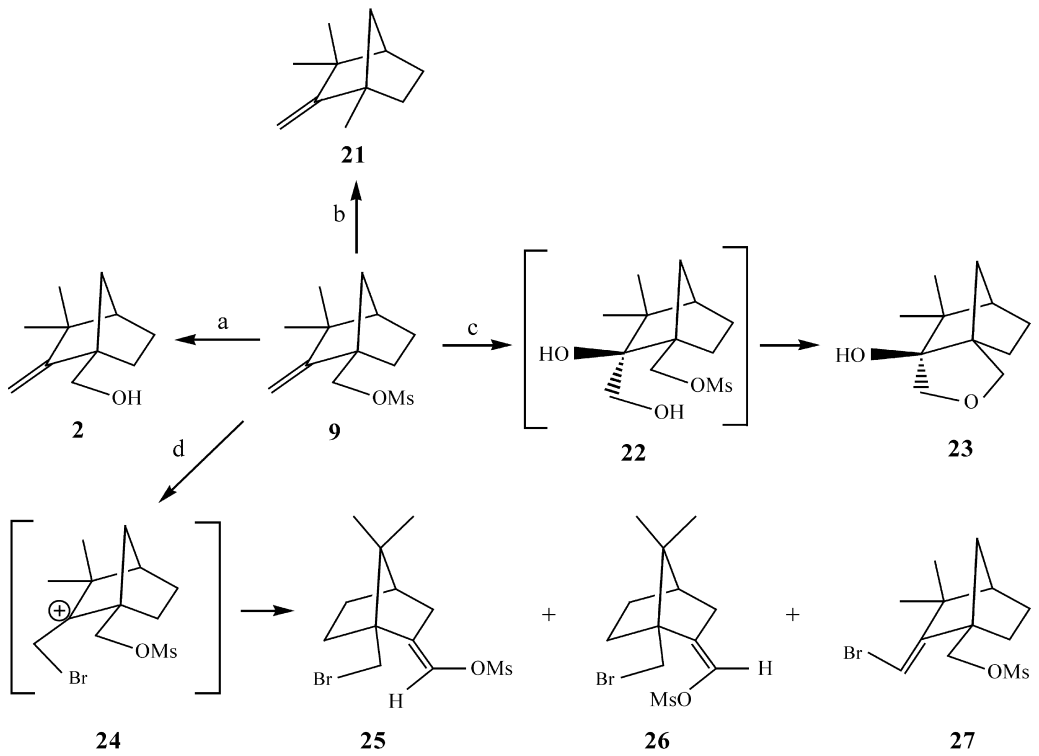
The reaction of (+)-camphor with methylene triphenylphosphorane gave 2-methylenebornane (**10**, Scheme 1), which is a known alkene derivative.[15,16] Oxidation of **10** with TMO, using OsO_4 (1% equiv.) as the catalyst, afforded isoborneols **11** and **12** in 75% yield with ratio of 7:1. Although both **11** and **12** are also known compounds, they used to be obtained as a mixture in low yield (46%) and poor efficiency (4 days) from a reaction[16] in which expensive osmium tetroxide had been stoichiometrically employed as the oxidant instead of catalyst. Surprisingly, separate treatments of **11** and **12** with MsCl in the presence of triethylamine predominantly provided **9** in good yield[17] (84%). Presumbably, once compound **13** or **14** was produced at the beginning of each reaction, an unexpected dehydration occurred in situ immediatedly such that carbonium ion **15** was formed. Overall, Wagner–Meerwein rearrangement[14] of **11** and **12** individually furnished methanesulfonate **9**. Methylene bornane derivative **16** (14%) was the minor product given by the reaction, and isolated as a mixture of geometric isomers. The dehydration on **13** and **14** might be further proved with the existence of **16** (*E*/*Z*=2:1). It is noteworthy that a rearrangement product (**9**) was formed predominantly over an elimination product (**16**) via carbonium ion **15**, whereas an elimination product (**19**) was formed predominantly over a rearrangement product (**20**) via carbonium ion **18**, which was derived from homoallylic alcohol **17** as shown in Scheme 2.[18]



Scheme 2. Ref. 18.

A series of interesting reactions of **9** is now shown in Scheme 3. Hydrolysis of **9** with 4N KOH gave fenchyl alcohol **2**, which is a key enantiomeric intermediate[3] for the synthesis of sesquiterpenoids and used to be prepared via another procedure in low yield.[2] Methylene fenchone **21**, the enantiomer of intermediate for ethyl fenchols,[19] has been recently prepared by Thomas et al.,[14] starting from **8**. Indeed, reduction of **9** with lithium aluminum hydride instead of Super hydride[14] could also give **21** (in ~70% yield), although the product is somewhat volatile. The treatment of **9** with TMO in the presence of OsO_4 directly afforded hydroxytetrahydrofuran **23** (70%). It is postulated that dihydroxylation of vinyl group on **9** followed by intramolecular substitution of **22** in situ resulted in the formation of fenchyl analogue **23**. The structures of both **9** (Fig. 2) and **23** (Fig. 3) were confirmed by X-ray analysis. To the best of our knowledge, **23** is a new analogue of the class of oxatricyclo compounds.[18–22] Finally, methanesulfonate **9** did undergo further Wagner–Meerwein rearrangement in the reaction with NBS to provide new methylene camphor analogues **25** and **26** as the major products in 75% yield with ratio of 2:1.

That methanesulfonate **27** was also produced (in 13% yield) may prove that carbonium ion **24** was formed before the



Scheme 3. (a) KOH, EtOH, reflux, 40 h; (b) $LiAlH_4$, ether, reflux; (c) TMO, OsO_4, Py, *t*-BuOH, H_2O; (d) NBS, CH_2Cl_2, rt.

rearrangement occurred. Both compound **25** and compound **26** are new analogues of 2-methylenebornane. Their applications are under investigation and the results will be reported in due course.

In conclusion, the preparation of a new and useful chiral fenchone analogue (**9**) has been described. Methanesulfonate **9** was obtained stereospecifically and straightforwardly. This compound is a key and versatile intermediate, and is multiple useful for the syntheses of several products belonging to various classes.

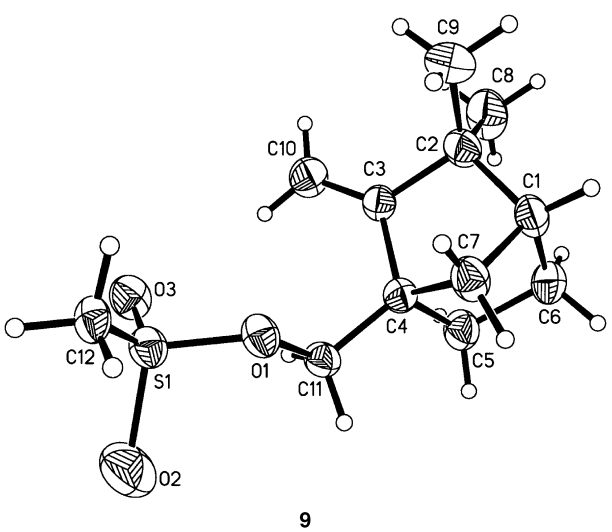


Figure 2.

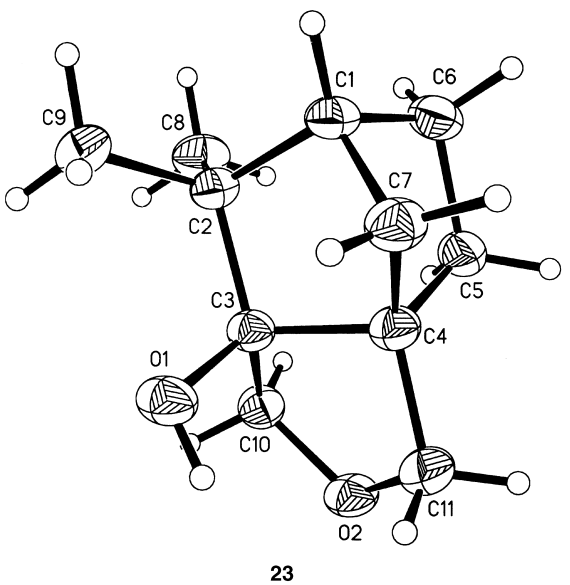


Figure 3.

3. Experimental

3.1. Data for compounds

3.1.1. (+)-3,3-Dimethyl-2-methylenenorbornan-1-yl methanol (2). To a solution of **9** (0.30 g, 1.2 mmol) in EtOH (10 ml) was added 4N KOH (6 ml). The reaction mixture was heated at reflux for 40 h, then neutralized with 3N HCl. The mixture was extracted with CH_2Cl_2 (3×10 ml).

The organic layers were combined and washed with brine and water, then dried ($MgSO_4$), filtered and concentrated under reduced pressure. The residue was purified with silica gel column chromatography (5:1, *n*-hexane/EtOAc) to give **2** (0.17 g, 83%) as a syrup. $[\alpha]_D^{25}$=+43.5 (0.10, CH_2Cl_2); IR (film) 3416 (br), 3071, 1652 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 1.03 (s, 3H), 1.07 (s, 3H), 1.12–1.27 (m, 2H), 1.51–1.55 (m, 2H), 1.71–1.80 (m, 3H), 1.88 (br s, 1H), 3.69 (d, *J*=11.4 Hz, 1H), 3.91 (d, *J*=11.4 Hz, 1H), 4.64 (s, 1H), 4.66 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 24.60, 25.91, 29.15, 30.99, 39.53, 43.24, 46.91, 56.21, 63.83, 98.38, 165.28.

3.1.2. (+)-(3,3-Dimethyl-2-methylenenorbornan-1-yl)-methyl methanesulfonate (9) and methane-sulfonate 16. To a solution of **11** (2.30 g, 12.5 mmol) in dichloromethane (50 ml) was added triethylamine (1.80 g, 18.8 mmol) at 0°C. After the solution was stirred for 30 min., methanesulfonyl chloride (2.10 g, 18.8 mmol) was added. The reaction mixture was stirred for 3 h at room temperature, then quenched with water (15 ml) at 0°C. The organic layer was washed with more water (3×15 ml), dried (Na_2SO_4), and concentrated under reduced pressure. The residue was purified with silica gel column chromatography (5:1, *n*-hexane/EtOAc) to give **9** (2.52 g, 84%) and **16** (0.42 g, 14%) as colorless solids. Data of **9**: $[\alpha]_D^{25}$=+55.58 (0.13, CH_2Cl_2); mp 40–41°C; IR (KBr) 3080, 1660, 1354, 1170 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 1.04 (s, 3H), 1.09 (s, 3H), 1.20–1.92 (m, 7H), 3.03 (s, 3H), 4.40 (d, *J*=10.0 Hz, 1H), 4.46 (d, *J*=10.0 Hz, 1H), 4.64 (s, 1H), 4.66 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 24.60, 25.88, 29.28, 30.65, 37.14, 40.00, 43.19, 47.02, 52.96, 71.15, 99.23, 163.85. Anal. calcd for $C_{12}H_{20}O_3S$: C, 58.98; H, 8.25; S, 13.12. Found: C, 58.89; H, 8.35; S, 13.05.

Data of **16** (mixture of *E* and *Z*-forms): ^1H NMR (200 MHz, $CDCl_3$): δ 0.78 (s, 3H), 0.84 (s, 3H), 0.87 (s, 3H), 0.91 (s, 3H), 0.97 (s, 3H), 1.21 (s, 3H), 1.25–1.95 (m, 12H), 2.34–2.54 (m, 2H), 3.02 (s, 3H), 3.03 (s, 3H), 6.28 (t, *J*=2.6 Hz, 1H), 6.34 (t, *J*=2.2 Hz, 1H). Anal. calcd for $C_{12}H_{20}O_3S$: C, 58.98; H, 8.25; S, 13.12. Found: C, 59.13; H, 8.20; S, 12.73.

3.1.3. (1*R*,2*S*)-2-(Hydroxymethyl)-1,7,7-trimethyl-bicyclo-[2.2.1]heptan-2-ol (11) and (1*R*,2*R*)-2-(hydroxymethyl)-1,7,7-trimethyl- bicyclo-[2,2,1]heptan-2-ol (12). To a mixture of **10** (5.00 g, 33.3 mmol), trimethylamine *N*-oxide (5.60 g, 49.9 mmol) in *tert*-butanol (75 ml), water (10 ml) and pyridine (3.75 ml) was added dropwise osmium tetroxide (2.5% in *t*-BuOH, 3.36 ml, 0.33 mmol). The reaction mixture was heated at reflux for 15 h, then cooled to room temperature and quenched with sodium bicarbonate (20%, 50 ml). The mixture was extracted with petroleum ether (3×50 ml). The organic layers were combined and washed with water (3×50 ml), dried (Na_2SO_4), and concentrated under reduced pressure. The residue was purified with silica gel column chromatography (3:1, *n*-hexane/EtOAc) to give **11** (5.46 g, 65.6%) and **12** (0.77 g, 9.4%) as colorless solids. Data of **11**: $[\alpha]_D^{27}$= −36.7 (0.12, CH_2Cl_2); mp 199–200°C; IR (KBr) 3435 (br) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 0.81 (s, 3H), 0.91 (s, 3H), 0.92 (s, 3H), 1.13–1.36 (m, 2H), 1.68–1.79 (m, 2H), 2.01–2.18 (m, 3H), 2.28 (br s, 1H), 3.63 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 10.91, 21.23, 21.55, 26.82, 29.58, 42.46, 44.45, 49.30, 52.09, 69.31, 80.52. Calcd for $C_{11}H_{20}O_2$: C, 71.70; H, 10.94. Found: C, 71.60; H, 10.96.

Data of **12**: $[\alpha]_D^{27}$=+36.4 (0.11, CH_2Cl_2); mp 185–186°C; ^1H NMR (200 MHz, $CDCl_3$): δ 0.85 (s, 3H), 0.93 (s, 3H), 1.04 (m, 1H), 1.25–1.55 (m, 3H), 1.65 (br s, 1H), 1.76 (m, 1H), 1.89–2.05 (m, 2H), 2.24 (br s, 1H), 3.51 (dd, *J*=6.2, 10.6 Hz, 1H), 3.66 (dd, *J*=4.4, 10.6 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 11.21, 20.29, 21.13, 26.98, 30.07, 43.62, 44.76, 49.62, 51.12, 68.92, 80.69.

3.1.4. (+)-1-Methyl-3,3-dimethyl-2-methylene-bicyclo-[2.2.1]heptane (21). Methanesulfonate **9** (0.5 g, 2.1 mmol) in ether (5 ml) was added dropwise to a solution of lithium aluminum hydride (0.1 g, 2.7 mmol). The reaction mixture was refluxed for 3 h, then cooled to room temperature and quenched with ice water. After the solvent was evaporated, the product was purified with silica gel column chromatography (hexane) to give **21**[14] (0.2 g, 70%) as a colorless oil; IR (film) 3071, 1651 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 1.01 (s, 3H), 1.06 (s, 3H), 1.18 (s, 3H), 1.26 (m, 1H), 1.40–1.56 (m, 4H), 1.68–1.74 (m, 1H), 1.82 (br s, 1H), 4.53 (s, 1H), 4.60 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 18.34, 25.47, 26.15, 29.56, 35.58, 42.81, 44.30, 47.37, 49.94, 96.94, 169.34.

3.1.5. Hydroxyl tetrahydrofuran 23. Compound **9** (0.5 g, 2.1 mmol), trimethylamine *N*-oxide (1.2 g, 10.7 mmol), pyridine (2 ml), *tert*-butanol (20 ml), and water (3 ml) were added to a round bottom flask. To the solution was added dropwise osmium tetroxide (0.62 ml, 2.5 wt% in 2-methyl-2-propanol, 0.06 mmol). The mixture was heated at reflux for 16 h, then cooled to room temperature. The reaction was quenched with 20% $NaHCO_3$ (10 ml) and extracted with petroleum ether (3×20 ml). The organic layers were combined and washed with water, dried (Na_2SO_4), and concentrated under reduced pressure. The residue was purified with silica gel column chromatography (3:1, *n*-hexane/EtOAc) to give **23** (0.29 g, 70%) as a white solid. $[\alpha]_D^{27}$=−24.9 (0.13, CH_2Cl_2); mp 141–142°C; IR (KBr) 3442 (br) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 1.00 (s, 3H), 1.10 (s, 3H), 1.22–2.17 (m, 7H), 3.45 (d, *J*=8.6 Hz, 1H), 3.63 (d, *J*=7.2 Hz, 1H), 3.91 (d, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 23.47, 24.98, 25.43, 30.98, 34.08, 39.24, 55.12, 61.59, 69.21, 69.21, 93.06. Anal. calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.43; H, 9.72.

3.1.6. Reaction of compound 9 with NBS. To a solution of **9** (0.80 g, 3.3 mmol) in CH_2Cl_2 (10 ml) was added dropwise a mixture of *N*-bromosuccinimide (0.80 g, 4.5 mmol) and pyridine (2.5 ml) in CH_2Cl_2 (10 ml) at 0°C. The reaction mixture was stirred at room temperature for 16 h. Hexane was then added to the mixture to form a precipitate. The suspension was filtered, and the filtrate was concentrated under reduced pressure. The residue was purified with silica gel column chromatography (6:1, *n*-hexane/EtOAc) to give **25** (0.46 g, 43%) as a syrup, **26** (0.22 g, 21%) as a syrup and **27** (0.12 g, 11%) as a syrup. Data of **25**: $[\alpha]_D^{26}$=−80.3 (0.10, CH_2Cl_2); IR (film) 3059, 1685, 1369, 1181, 525 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 0.86 (s, 3H), 0.97 (s, 3H), 1.27 (m, 1H), 1.65 (m, 1H), 1.83 (m, 3H), 2.00 (dd, *J*=17.0, 2.4 Hz, 1H), 2.57 (m, 1H), 3.04 (s, 3H), 3.48 (d, *J*=10.6 Hz, 1H), 3.54 (d, *J*=10.6 Hz, 1H), 6.78 (t, *J*=2.6 Hz, 1H); ^{13}C

NMR (50 MHz, $CDCl_3$): δ 18.94, 19.94, 27.07, 32.83, 33.19, 33.59, 37.14, 45.44, 50.59, 53.91, 127.66, 138.63. Anal. calcd for $C_{12}H_{19}O_3BrS$: C, 44.59; H, 5.92; S, 9.92. Found: C, 44.90; H, 5.98; S, 9.71. Data of **26**: $[\alpha]_D^{26}=17.6$ (0.10, CH_2Cl_2); IR (film) 3065, 1686, 1371, 1178, 517 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 0.94 (s, 3H), 0.95 (s, 3H), 1.21 (m, 1H), 1.53 (m, 1H), 1.75–1.92 (m, 4H), 2.44 (m, 1H), 3.09 (s, 3H), 3.69 (d, J=10.8 Hz, 1H), 3.77 (d, J=10.8 Hz, 1H), 6.41 (t, J=2.0 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 18.82, 21.15, 26.99, 33.05, 33.39, 34.29, 37.43, 45.73, 50.09, 55.57, 126.87, 132.37. Anal. calcd for $C_{12}H_{19}O_3BrS$: C, 44.59; H, 5.92; S, 9.92. Found: C, 44.86; H, 6.11; S, 9.47.

Data of **27**: $[\alpha]_D^{26}=+114.6$ (0.10, CH_2Cl_2); IR (film) 3066, 1730, 1361, 1176, 528 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 1.27 (s, 3H), 1.33 (s, 3H), 1.37 (m, 1H), 1.61 (m, 2H), 1.75 (m, 2H), 1.91 (m, 2H), 3.03 (s,3H), 4.34 (d, J=10.2 Hz, 1H), 4.41 (d, J=10.2 Hz, 1H), 5.81 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 23.05, 23.86, 24.47, 30.68, 37.24, 39.71, 45.07, 48.92, 55.91, 70.38, 94.49, 156.02. Anal. calcd for $C_{12}H_{19}O_3BrS$: C, 44.59; H, 5.92; S, 9.92. Found: C, 44.99; H, 5.91; S, 9.46.

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