Tetrahedron 65 (2009) 9884–9896

Contents lists available at ScienceDirect

Tetrahedron

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

Intramolecular Friedel–Crafts type reaction of vinyloxiranes linked to an ester group

Shinji Nagumo [a,*], Toshie Miura [b], Megumi Mizukami [b], Irie Miyoshi [b], Masanori Imai [b], Norio Kawahara [b], Hiroyuki Akita [c]

[a] Department of Applied Chemistry, Kogakuin University, Nakano 2665-1, Hachioji, Tokyo 192-0015, Japan
[b] Hokkaido Pharmaceutical University, School of Pharmacy, Katsuraoka 7-1, Otaru 047-0264, Japan
[c] School of Pharmaceutical Science, Toho University, 2-2-1 Miyama, Funabashi, Chiba 274-8510, Japan

ARTICLE INFO

Article history:
Received 21 May 2009
Received in revised form 7 September 2009
Accepted 8 September 2009
Available online 12 September 2009

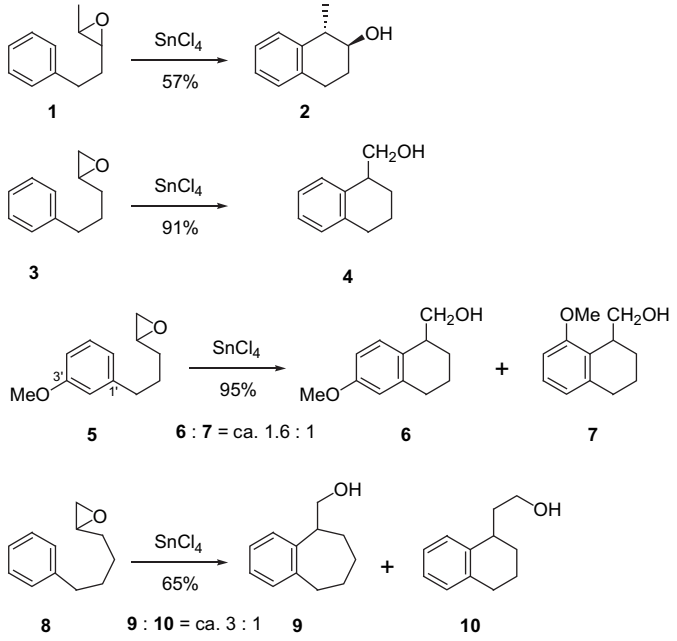
ABSTRACT

The 7-*endo* Friedel–Crafts cyclization of arylpropyl vinyloxiranes was found to proceed regio- and stereoselectively to afford polyfunctional seven-membered carbocycles in excellent yields.

© 2009 Elsevier Ltd. All rights reserved.

1. Introduction

Ring opening reaction of epoxide with various nucleophiles continues to be used for the synthesis of many natural products. Epoxide can react in either of two directions distinct from other functional groups. Consequently, it is important to control the reaction site of the substitution. The regioselectivity of epoxides is mainly determined by a steric factor, stereoelectronic requirement, and/or the fractional positive charge of the carbon center in the transition state. An intramolecular reaction of epoxides is also regulated by ring size of products in addition to the above factors. Taylor et al. investigated an intramolecular Friedel–Crafts (FC) reaction of arylalkyl epoxides mediated by various acids.[1–3] Their study indicated that six-membered FC cyclization was favored over five- and seven-membered FC cyclization. Furthermore, 6-*exo* cyclization seemed to be more facile than 6-*endo* cyclization. Secondary epoxide **1** undertook 6-*endo* cyclization to give alcohol **2** in moderate yield (Scheme 1). On the other hand, an excellent yield was obtained from the 6-*exo* cyclization of **3**. Cyclization of epoxide **5** having a substituent at the C3′-position resulted in the formation of *para*- and *ortho*-substitution products **6** and **7** with a ratio of ca. 1.6:1. Homologous epoxide **8** underwent seven-membered cyclization to form **9** in moderate yield. It is of good synthetic potential because there are many natural and medicinal compounds containing a seven-membered carbocycle with a polyfunctional group. However, seven-membered cylization of simple epoxide is limited to *exo* mode. Our attention has thus been directed to the development of a facile method of 7-*endo*-selective FC cyclization.



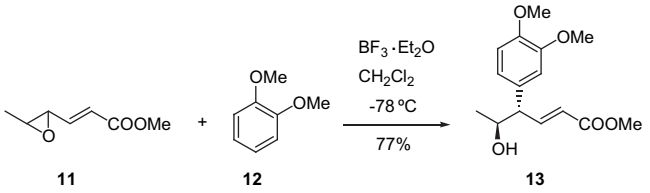
Scheme 1.

Linkage of a functional group exerting a resonance effect is known to be useful for controlling the reaction site of epoxide.[4,5] Akita et al. reported intermolecular FC reaction of γ,δ-epoxy-α,β-unsaturated ester **11** with arene derivatives upon treatment with $BF_3 \cdot Et_2O$ (Scheme 2).[6] In their research, arene derivatives selectively attacked the epoxide carbon linked to the vinyl group. Such

* Corresponding author.
E-mail address: bt13071@ns.kogakuin.ac.jp (S. Nagumo).

0040-4020/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2009.09.037

a resonance effect would make 7-*endo* FC cyclization of epoxides more advantageous than 6-*exo* FC cyclization. We report here 7-*endo*-selective FC cyclization of arylalkyl vinyloxiranes.[7]

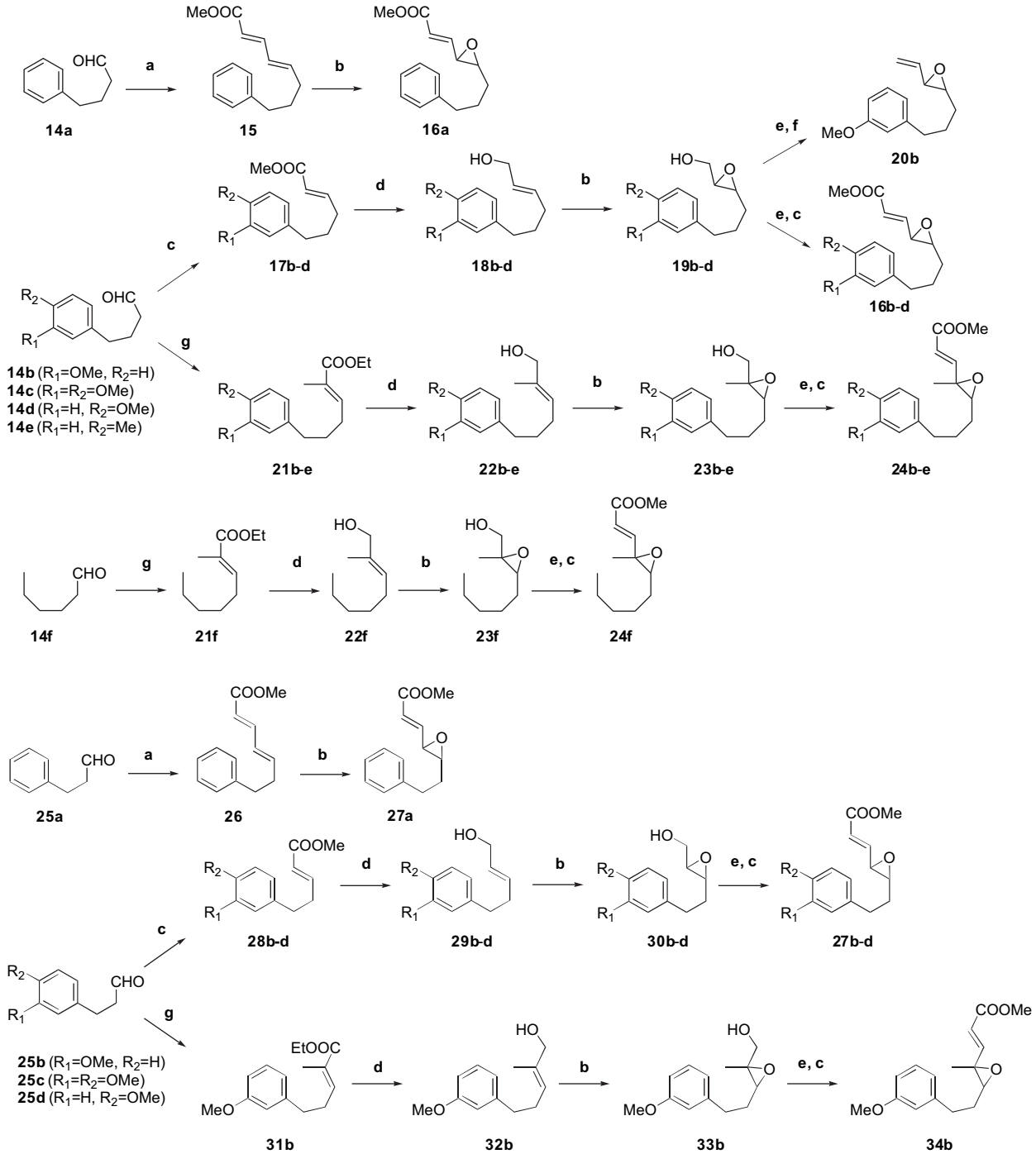


Scheme 2.

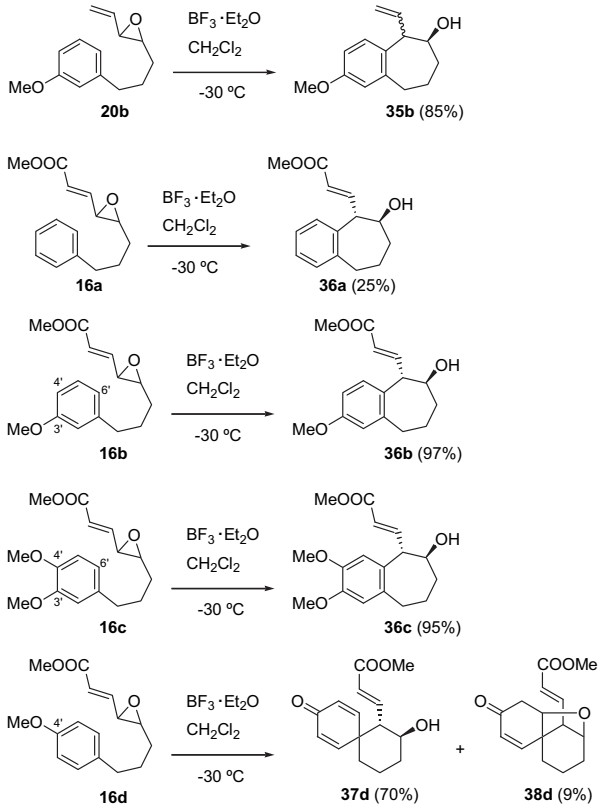
2. Results

2.1. Synthesis of vinyloxiranes

Vinyloxiranes **16a–d**, **20b**, and **24b–f** were synthesized from the corresponding aldehydes **14a–f** (Scheme 3). Horner–Emmons reaction of **14a** with $(EtO)_2POCH_2CH{=}CHCOOMe$ gave ester **15**, which was converted into **16a** by epoxidation with MCPBA. Wittig reaction of **14b–f** with $Ph_3P{=}CHCOOMe$ or $Ph_3P{=}CMeCOOEt$ produced conjugate esters **17b–d** or **21b–f**, respectively. Reduction of **17b–d** and **21b–f** with DIBAL-H afforded the corresponding allylalcohols **18b–d** and **22b–f**, which were subjected to epoxidation with MCPBA to give epoxyalcohols **19b–d** and **23b–f**. Finally,



Scheme 3. (a) $(EtO)_2POCH_2CH{=}CHCOOMe$, LDA, THF; (b) MCPBA, CH_2Cl_2; (c) $Ph_3P{=}CHCOOMe$, THF; (d) DIBAL-H, toluene, −78 °C; (e) Dess–Martin periodinane, CH_2Cl_2; (f) Ph_3PCH_3Br, KHMDS, THF, −20 °C, (g) $Ph_3P{=}CMeCOOEt$, THF.

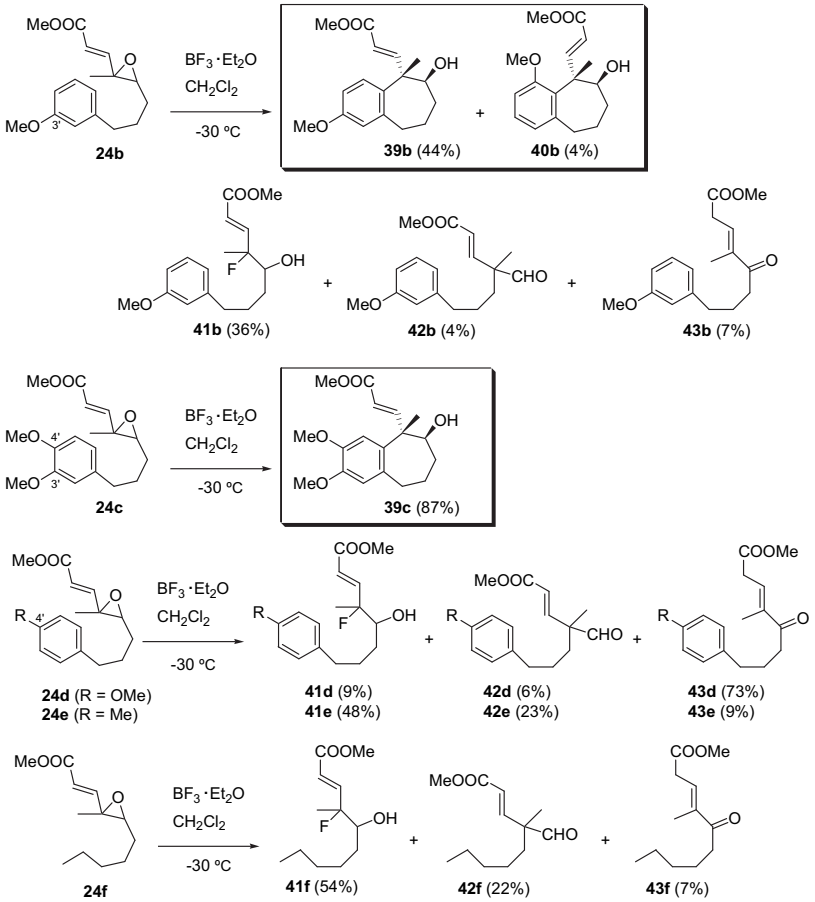


Scheme 4.

19b–d and **23b–f** were converted into **20b**, **16b–d** and **24b–f** by the sequence of Dess–Martin oxidation and Wittig reaction. Conversion of **25a–d** into **27a–d** and **34b** was also carried out in a manner similar to that described above.

2.2. 7-*endo*-Selective cyclization of vinyloxiranes

As the start of this research, we performed FC cyclization of vinyloxirane **20b**, in which 7-*endo* versus 6-*exo* cyclization can competitively occur (Scheme 4). As was expected, the regiochemical outcome was guided by the vinyl group and 7-*endo* cyclization was favored over 6-*exo* cyclization. Treatment of vinyloxirane **20b** with 0.5 equiv of $BF_3 \cdot Et_2O$ in CH_2Cl_2 at $-30\,^{\circ}C$ afforded seven-membered carbocycle **35b** in 85% yield as an epimeric mixture. In contrast to the above reaction, selective 7-*endo* cyclization of vinyloxirane **16a** with an ester group proceeded stereoselectively to afford only trans isomer **36a**, but its yield was very low. Substitution of a simple epoxide is known to proceed with inversion of configuration. Such a special stereochemistry of epoxide can be ascribed to the neighboring effect of epoxide-oxygen on the reaction center in an intermediate or a transition state.[1] However, the cyclization of **20b** can be considered to proceed via an almost open cation that is not subjected to the neighboring effect. The S_N1-like mechanism depends on the strong resonance effect by vinyl groups. Ester group in **16a** should moderately decrease the resonance effect of the vinyl group toward epoxide. Activation by methoxy group made the 7-*endo* cyclization more facile. Vinyloxiranes **16b** and **16c** underwent facile 7-*endo* cyclizations at only 6′-positions to produce **36b** and **36c**, respectively, in excellent yield. On the other hand, vinyloxirane **16d** having only a methoxy group at the 4′-position was surprisingly transformed into the spiro-cyclic



Scheme 5.

product **37d** and its intramolecular 1,4-adduct **38d** under acidic conditions.

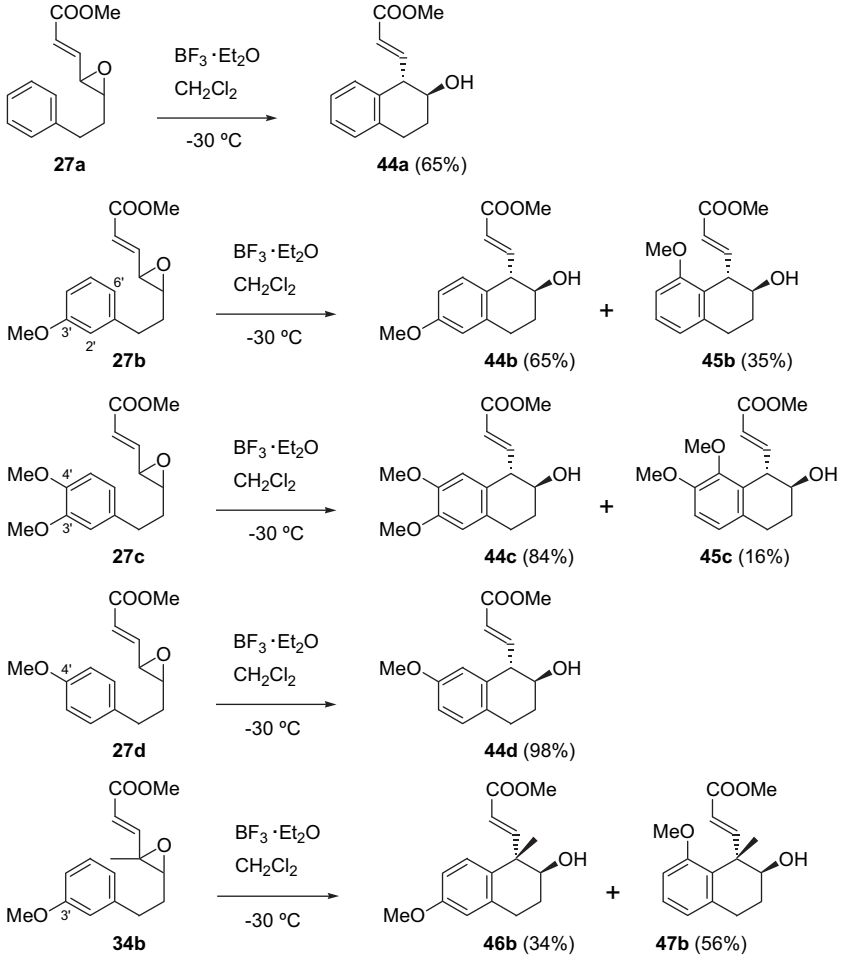
We next turned our attention to explore the behavior of trisubstituted epoxides linked to conjugate ester under acidic conditions (Scheme 5). It is well-known that trisubstituted epoxides undergo facile 1,2-alkyl or 1,2-hydride migration upon treatment with Lewis acids.[8] Treatment of vinyloxirane **24b** with $BF_3 \cdot Et_2O$ afforded two regioisomers **39b** and **40b** in 44% and 4% yields along with fluorohydrin **41b** (36%),[9] aldehyde **42b** (4%), and ketone **43b** (7%).[10] The unsatisfactory result could be modified by introduction of a further methoxy group at the C4′-position. Upon treatment with $BF_3 \cdot Et_2O$, **24c** was converted into seven-membered carbocycle **39c** in high yield. As well as cyclization of the secondary vinyloxirane, a methoxy group at the C3′-position was found to be essential for smooth 7-*endo* cyclization. Treatment of **24d** having a methoxy group at the C4′-position with $BF_3 \cdot Et_2O$ produced only undesired compounds: fluorohydrin **41d** (9%), aldehyde **42d** (6%), and ketone **43d** (73%).[10] It was noteworthy that the yield of ketone **43d** was higher than that of fluorohydrin **41d** in contrast to the result for **24b**. In order to clarify the reason for the difference, we performed $BF_3 \cdot Et_2O$-mediated reaction of vinyloxirane **24e** having a methyl group at the C4′-position and **24f** without a benzene ring. Interestingly, the ratio of fluorohydrins **41e**,**f**, aldehydes **42e**,**f**, and ketones **43e**,**f**[10] turned out to be comparable to that shown by the reaction of **24b**.

2.3. 6-*endo* Cyclization of vinyloxiranes

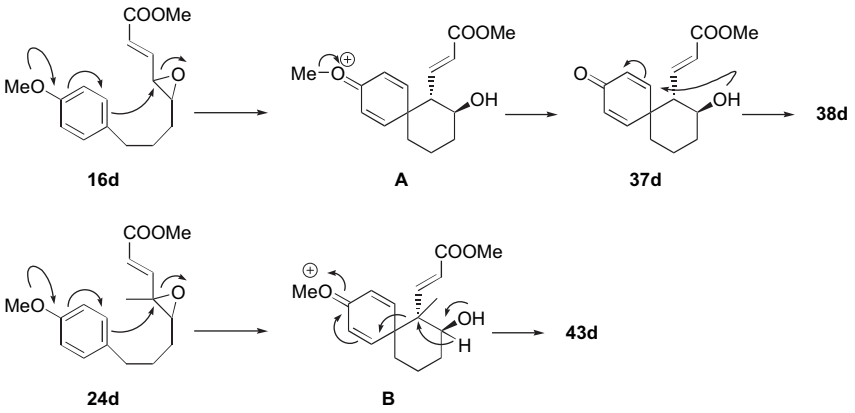
It should be noted that vinyloxiranes **16b** underwent cyclization at the C6′-position specifically, since six-membered cyclization of simple epoxide **5** proceeded at both C2′ and C6′-positions. We considered that it would be instructive to conduct 6-*endo* FC cyclization of 4,5-epoxy-7-aryl-2-heptenoates. Treatment of vinyloxirane **27a** with 0.5 equiv of $BF_3 \cdot Et_2O$ in CH_2Cl_2 at −30 °C resulted in 6-*endo* cyclization yielding tetrahydro-2-naphthol **44a** in moderate yield (Scheme 6). The 6-*endo* cyclization of vinyloxirane **27b** proceeded at both the 2′ and 6′-positions to afford **44b** and **45b** in combined yield of 100% and a ratio of ca. 2:1. Also, cyclization of **27c** proceeded smoothly at both the 2′ and 6′-positions to produce **44c** and **45c** with a ratio of ca. 5:1. Interestingly, **27d** possessing only a methoxy group at the C4′-position afforded fused ring compound **44d** in contrast to the result for **16d**. When trisubstituted epoxide **34b** with a 3′-methoxy group was treated with $BF_3 \cdot Et_2O$, **46b** and **47b** were obtained in combined yield of 90% and a ratio of ca. 2:3.

3. Discussion

As we expected, 7-*endo* cyclization of vinyloxirane was favored over 6-*exo* cyclization due to resonance control by the vinyl group. The *endo*-selective cyclization was also applicable to six-membered cyclization. Several differences between 6-*endo* and 7-*endo* cyclizations should be considered. Vinyloxirane **27d** having a methoxy group at the C4′-position undergoes FC cyclization to afford **44d** in excellent yield (Scheme 6), whereas **16d** undergoes *ipso*-cyclization and the subsequent demethylation of the resulting spiro-benzenium ion **A** to afford spiro-cyclic products **37d** and **38d** (Schemes 4 and 7). It is also noteworthy that trisubstituted epoxides **24e**,**f** give mainly fluorohydrins **41e**,**f** and aldehydes **42e**,**f**, whereas **24d** having a methoxy group at the C4′-position gives ketone **43d** as



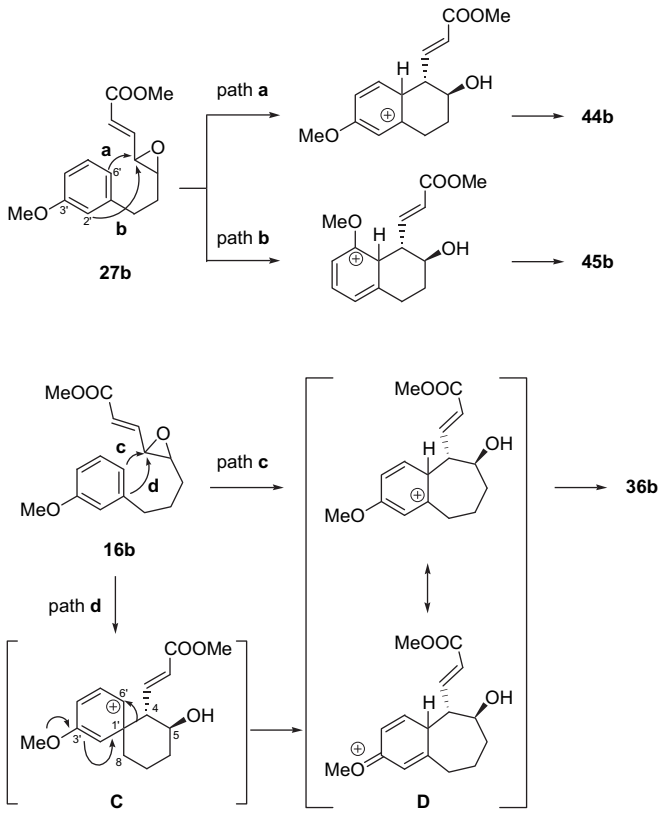
Scheme 6.



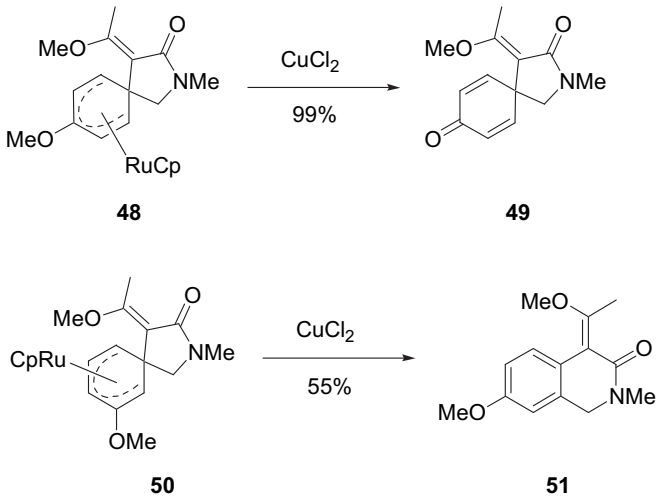
Scheme 7.

a major product (Scheme 5). Selective formation of **43d** might be ascribed to the temporary formation of spiro-benzenium ion **B** (Scheme 7) and its 1,2-hydride migration concomitant with aromatization.

Interestingly, positional selectivity on the benzene ring shows a remarkable difference between 6-*endo* cyclization and 7-*endo* cyclization. Thus, 6-*endo* cylizations of **27b**,**c** provide C6′-cyclized products **44b**,**c** and C2′-cyclized products **45b**,**c**, whereas 7-*endo* cyclizations of **16b**,**c** proceed regioselectively to afford only C6′-cyclized products **36b**,**c** in excellent yield (Schemes 4 and 6). Generally, two pathways are possible for intramolecular FC cyclization of various electrophilic functional groups: direct cyclization at the position *ortho* to the alkyl side chain and a sequential mechanism via a spiro-benzenium ion. A kinetic study by Taylor et al. revealed that 6-*exo* cyclization of simple epoxide **3** and its derivatives occurred almost completely via a direct route (Scheme 1).[1–3] Among of the derivatives, epoxide **5** possessing a methoxy group at the C3′-position underwent cyclization at both the C2′ and C6′-positions to afford **6** and **7** with a ratio of ca. 1.6:1. Interestingly, the ratio is close to that of **44b** and **45b**, which were obtained in FC cyclization of vinyloxirane **27b**. The similarity of their ratios suggests that 6-*endo* cyclization of vinyloxirane **27b** also prefers direct routes (Scheme 8, paths a and b). Of course, also 7-*endo* cyclization of **16b** should be considered to proceed via a direct route (Scheme 8, path c). However, strange to say for this mechanistic insight is that the direct cyclization at the C2′-position does not occur in contrast to the 6-*endo* cyclization. We thus think that it is difficult to rule out the following possibility. As well as the reaction of **16d** and **24d** (Scheme 7), **16b** might undergo *ipso*-cyclization to generate a spiro-benzenium ion (Scheme 8, path d). In contrast with **A** and **B** (Scheme 7), the cation **C** contains a methoxy group at the C3′-position. Electron-releasing by the substituent may induce the subsequent skeletal rearrangement to afford the ion **D**, which is converted into seven-membered carbocycle **36b**. If so, the complete regioselectivity on the benzene ring for the cyclization of **16b** would be ascribed to selective migration of the C4–C1′ bond to the C4–C6′ bond. Although the reason for this remains unclear, a similar selectivity of migration was reported by Pigge et al. in a skeletal rearrangement of azaspiro cyclohexadienyl ruthenium complex **50** concomitant with a demetalation (Scheme 9).[11] On the other hand, the demetalation of **48** underwent demethylation concomitantly to produce the spiro-cyclic compound **49** as well as $BF_3 \cdot Et_2O$-promoted reaction of **16d**.



Scheme 8.



Scheme 9.

4. Conclusion

In conclusion, we have developed a facile 7-*endo*-selective FC cyclization of vinyloxiranes mediated by $BF_3 \cdot Et_2O$. Each cyclization

exhibited excellent stereoselectivity. This novel method was also applicable to a six-membered cyclization. The positional selectivity on the benzene ring showed a remarkable difference between 6-*endo* cyclization and 7-*endo* cyclization. Thus, 6-*endo* cyclization of **27b**,**c** provide two regiochemical isomers, whereas 7-*endo* cyclizations of **16b**,**c** proceed regioselectively. Seven-membered products obtained from 7-*endo*-selective FC cyclization of vinyloxiranes should be useful for synthetic applications because they have polyfunctional groups.

5. Experimental

5.1. General methods

The melting points were determined on a Yanako micro melting point apparatus and were uncorrected. IR spectra were recorded on a JASCO IRA-102 or a JASCO FT-IR-7000 spectrometer. NMR spectra were recorded on a JEOL GX-270 and a JEOL AL-400 spectrometer using tetramethylsilane as an internal standard. Chemical shifts are given in parts per million. The following abbreviations are used: s, singlet; d, doublet; t, triplet; q, quartet; br, broad. MS spectra were measured on a Hitachi M-2000 instrument. Elemental analyses were performed using a Perkin Elmer 2400II. Column chromatography was carried out on Merck's Silica gel 60 (70–230 mesh ASTM).

5.2. Horner–Emmons reaction of 14a and 25a

To a solution of $(EtO)_2POCH_2CH{=}CHCOOMe$ (1.1 equiv) in THF was added dropwise LDA (1.1 equiv) in THF at −78 °C under an argon atmosphere. After being stirred for 10 min, a solution of **14a** or **25a** in THF was added to the mixture. After 1 h, the reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with Et_2O. The extract was washed with saturated aqueous NaCl, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluted with hexane/AcOEt (30/1) to give diene conjugate ester **15** or **26**.

*5.2.1. Methyl (2E,4E)-8-phenylocta-2,4-dienoate (**15**).* Yield 59% (colorless oil); IR (neat) 1717, 1644 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 7.35–7.15 (6H, m), 6.25–6.05 (2H, m), 5.79 (1H, d, J=15.5 Hz), 3.74 (3H, s), 2.63 (2H, t, J=7.6 Hz), 2.21 (2H, q, J=7.6 Hz), 1.76 (2H, quintet, J=7.6 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 167.60, 145.12, 144.08, 141.84, 128.67, 128.35 (2C), 128.89 (2C), 125.81, 118.88, 51.37, 35.25, 32.36, 30.26; EIMS m/z 230 (M^+), 199, 170, 147; HRMS (EI) m/z 230.1313 (calcd for $C_{15}H_{18}O_2$: 230.1306).

*5.2.2. Methyl (2E,4E)-7-phenylhepta-2,4-dienoate (**26**).* Yield 56% (white solid); mp 48–49 °C (hexane). Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.78; H, 7.46. Found: C, 77.98; H 7.57. IR (neat) 1715, 1647 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 7.38 (1H, dd, J=15.5, 10.8 Hz), 7.18–7.02 (3H, m), 6.98–6.90 (2H, m), 5.86–5.72 (2H, m), 5.62 (1H, dt, J=15.5, 7.6 Hz), 3.44 (3H, s), 2.37 (2H, t, J=7.6 Hz), 2.06 (2H, q, J=7.6 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 167.44, 144.90, 143.19, 140.93, 128.76, 128.29 (2C), 128.25 (2C), 125.94, 119.09, 51.27, 34.93, 34.56; EIMS m/z 216 (M^+), 185, 175, 149; HRMS (EI) m/z 216.1140 (calcd for $C_{14}H_{16}O_2$: 216.1149).

5.3. Epoxidation of arylalkyldienoates

To a solution of **15** or **26** in CH_2Cl_2 was added *m*-chloroperbenzoic acid (1.5 equiv) at 0 °C. The mixture was stirred at room temperature for 1 h and then quenched with saturated aqueous $Na_2S_2O_3$ and extracted with Et_2O. The extract was washed with saturated aqueous NaCl, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluted with hexane/AcOEt (10/1) to give epoxy conjugate ester **16a** or **27a**.

5.3.1. Methyl (4R,5R*,2E)-4,5-epoxy-8-phenyl-2-octenoate (**16a**).* Yield 72% (colorless oil); IR (neat) 1729, 1661 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 7.38–7.13 (5H, m), 6.67 (1H, dd, J=15.5, 7.2 Hz), 6.11 (1H, d, J=15.5 Hz), 3.74 (3H, s), 3.20 (1H, d, J=7.2, 2.0 Hz), 2.90 (1H, td, J=5.6, 2.0 Hz), 2.67 (2H, t, J=7.6 Hz), 1.89–1.56 (4H, m); ^{13}C NMR (68 MHz, $CDCl_3$) δ 166.00, 144.91, 141.56, 128.30 (4C), 125.86, 123.03, 61.17, 56.07, 51.61, 35.34, 31.25, 27.38; EIMS m/z 246 (M^+), 228, 214, 187, 169, 149, 131, 117, 104, 92; HRMS (EI) m/z 246.1245 (calcd for $C_{15}H_{18}O_3$: 246.1255).

5.3.2. Methyl (4R,5R*,2E)-4,5-epoxy-7-phenyl-2-heptenoate (**27a**).* Yield 72% (colorless oil); IR (neat) 1725, 1661, 1605 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 7.33–7.14 (5H, m), 6.63 (1H, dd, J=15.8, 6.9 Hz), 6.05 (1H, dd, J=15.8, 0.7 Hz), 3.74 (3H, s), 3.13 (1H, dd, J=6.9, 1.8 Hz), 2.91 (1H, td, J=5.6, 1.8 Hz), 2.88–2.67 (2H, m), 2.04–1.82 (2H, m); ^{13}C NMR (68 MHz, $CDCl_3$) δ 165.98, 144.76, 140.68, 128.45 (2C), 128.29 (2C), 126.12, 123.08, 60.61, 56.37, 51.61, 33.62, 31.94; EIMS m/z 232 (M^+), 201, 173, 141, 128, 117, 105; HRMS (EI) m/z 232.1078 (calcd for $C_{14}H_{16}O_3$: 232.1099).

5.4. Wittig reaction of arylalkanal with $Ph_3P{=}CHCOOMe$

To a solution of aldehyde **14** or **25** in THF was added $Ph_3P{=}CHCOOMe$ or $Ph_3P{=}CMeCOOEt$ (1.5 equiv) at room temperature under an argon atmosphere. After being stirred at room temperature for 12–15 h, a large amount of hexane was added to the reaction mixture. The precipitate was removed by filtration. The filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluted with hexane/AcOEt (20–10/1) to give conjugate ester **17**, **21**, **28** or **31**.

*5.4.1. Methyl (2E)-6-(3-methoxyphenyl)-2-hexenoate (**17b**).* Yield 89% (colorless oil); IR (neat) 1723, 1659 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 7.20 (1H, t, J=7.8 Hz), 6.98 (1H, dt, J=15.9, 7.3 Hz), 6.80–6.70 (3H, m), 5.84 (1H, dt, J=15.9, 1.5 Hz), 3.79 (3H, s), 3.73 (3H, s), 2.62 (2H, t, J=7.3 Hz), 2.33 (2H, qd, J=7.3, 1.5 Hz), 1.79 (2H, quintet, J=7.3 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 167.07, 159.68, 149.06, 143.30, 129.33, 121.26, 120.82, 114.22, 111.16, 55.13, 51.39, 35.23, 31.58, 29.47; EIMS m/z 234 (M^+), 203, 174, 161; HRMS (EI) m/z 234.1245 (calcd for $C_{14}H_{18}O_3$: 234.1255).

*5.4.2. Methyl (2E)-6-(3,4-dimethoxyphenyl)-2-hexenoate (**17c**).* Yield 78% (colorless oil); IR (neat) 1723, 1659 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 6.99 (1H, dt, J=15.6, 7.1 Hz), 6.80 (1H, d, J=8.6 Hz), 6.73–6.67 (2H, m), 5.84 (1H, dt, J=15.6, 1.6 Hz), 3.87 (3H, s), 3.86 (3H, s), 3.73 (3H, s), 2.59 (2H, t, J=7.7 Hz), 2.25 (2H, qd, J=7.1, 1.6 Hz), 1.77 (2H, quintet, J=7.7 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 166.90, 148.99, 147.75, 147.15, 134.17, 121.12, 120.09, 111.62, 111.16, 55.77, 55.68, 51.22, 34.64, 31.44, 29.66; EIMS m/z 264 (M^+), 233, 204, 191; HRMS (EI) m/z 264.1331 (calcd for $C_{15}H_{20}O_4$: 264.1360).

*5.4.3. Methyl (2E)-6-(4-methoxyphenyl)-2-hexenoate (**17d**).* Yield 96% (colorless oil); IR (neat) 1721, 1659, 1613 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 7.08 (2H, d, J=8.6 Hz), 6.98 (1H, dt, J=15.5, 6.9 Hz), 6.83 (2H, d, J=8.6 Hz), 5.83 (1H, dt, J=15.5, 1.3 Hz), 3.79 (3H, s), 3.73 (3H, s), 2.58 (2H, t, J=7.6 Hz), 2.22 (2H, qd, J=7.6, 1.3 Hz), 1.75 (2H, quintet, J=7.6 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 167.09, 157.82, 149.20, 133.70, 129.27 (2C), 121.16, 113.77 (2C), 55.22, 51.38, 34.25, 31.53, 29.81; EIMS m/z 234 (M^+), 134, 121; HRMS (EI) m/z 234.1229 (calcd for $C_{14}H_{18}O_3$: 234.1255).

*5.4.4. Ethyl (2E)-6-(3-methoxyphenyl)-2-methyl-2-hexenoate (**21b**).* Yield 45% (colorless oil); IR (neat) 1711, 1653 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 7.24–7.16 (1H, m), 6.82–6.70 (4H, m), 4.19 (2H, q, J=7.3 Hz), 3.80 (3H, s), 2.62 (2H, t, J=7.3 Hz), 2.20 (2H, q, J=7.3 Hz), 1.81 (3H, d, 1.5 Hz), 1.78 (2H, quintet, J=7.3 Hz), 1.29 (3H, t, J=7.3 Hz);

^{13}C NMR (68 MHz, $CDCl_3$) δ 168.22, 159.68, 143.52, 141.69, 129.29, 128.18, 120.84, 114.22, 111.14, 60.41, 55.14, 35.49, 30.02, 28.14, 14.29, 12.40; EIMS *m*/*z* 262 (M^+), 216, 161; HRMS (EI) *m*/*z* 262.1547 (calcd for $C_{16}H_{22}O_3$: 262.1568).

*5.4.5. Ethyl (2E)-6-(3,4-dimethoxyphenyl)-2-methyl-2-hexenoate (**21c**).* Yield 100% (colorless oil); IR (neat) 1711, 1651, 1607 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 6.84–6.67 (4H, m), 4.19 (2H, q, *J*=7.1 Hz), 3.87 (3H, s), 3.86 (3H, s), 2.59 (2H, t, *J*=7.6 Hz), 2.20 (2H, q, *J*=7.6 Hz), 1.81 (3H, d, *J*=1.2 Hz), 1.76 (2H, quintet, *J*=7.6 Hz), 1.30 (3H, t, *J*=7.1 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 168.07, 148.73, 147.12, 141.63, 134.39, 127.99, 120.11, 111.64, 111.14, 60.28, 55.79, 55.69, 34.90, 30.21, 27.97, 14.16, 12.29; EIMS *m*/*z* 292 (M^+), 247, 218, 191; HRMS (EI) *m*/*z* 292.1643 (calcd for $C_{17}H_{24}O_4$: 292.1673).

*5.4.6. Ethyl (2E)-6-(4-methoxyphenyl)-2-methyl-2-hexenoate (**21d**).* Yield 100% (colorless oil); IR (neat) 1711, 1651 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.08 (2H, d, *J*=8.8 Hz), 6.82 (2H, d, *J*=8.8 Hz), 6.83–6.72 (1H, m), 4.19 (2H, q, *J*=7.3 Hz), 3.79 (3H, s), 2.59 (2H, t, *J*=7.6 Hz), 2.18 (2H, q, *J*=7.6 Hz), 1.80 (3H, d, *J*=1.3 Hz), 1.74 (2H, quintet, *J*=7.6 Hz), 1.29 (3H, t, *J*=7.3 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 167.82, 157.59, 141.53, 133.57, 128.99 (2C), 127.79, 113.48 (2C), 60.07, 54.81, 34.25, 30.13, 27.79, 14.01, 12.10; EIMS *m*/*z* 262 (M^+), 188, 160; HRMS (EI) *m*/*z* 262.1540 (calcd for $C_{16}H_{22}O_3$: 262.1568).

*5.4.7. Ethyl (2E)-2-methyl-6-(4-methylphenyl)-2-hexenoate (**21e**).* Yield 83% (colorless oil); IR (neat) 1711, 1653 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (2H, d, *J*=8.1 Hz), 7.06 (2H, d, *J*=8.1 Hz), 6.77 (1H, t, *J*=7.3 Hz), 4.19 (2H, q, *J*=7.1 Hz), 2.60 (2H, t, *J*=7.3 Hz), 2.32 (3H, s), 2.19 (2H, q, *J*=7.3 Hz), 1.81 (3H, s), 1.76 (2H, quintet, *J*=7.3 Hz), 1.29 (3H, t, *J*=7.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.86, 141.57, 138.50, 134.96, 128.80 (2C), 128.06 (2C), 127.87, 60.11, 34.79, 30.07, 27.90, 20.73, 14.07, 12.15; EIMS *m*/*z* 246 (M^+), 201, 172; HRMS (EI) *m*/*z* 246.1606 (calcd for $C_{16}H_{22}O_2$: 246.1619).

*5.4.8. Ethyl (2E)-2-methyl-2-octenoate (**21f**).* Yield 93% (colorless oil); IR (neat) 1715, 1653 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 6.76 (1H, tq, *J*=7.6, 1.3 Hz), 4.19 (2H, q, *J*=7.3 Hz), 2.16 (2H, q, *J*=7.6 Hz), 1.83 (3H, d, *J*=1.3 Hz), 1.52–1.20 (6H, m), 1.30 (3H, t, *J*=7.3 Hz), 0.90 (3H, t, *J*=6.9 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 167.97, 142.12, 127.49, 60.08, 31.38, 28.44, 28.11, 22.31, 14.06, 13.73, 12.05; EIMS *m*/*z* 184 (M^+), 141, 109, 97, 83; HRMS (EI) *m*/*z* 184.1468 (calcd for $C_{11}H_{20}O_2$: 184.1462).

*5.4.9. Methyl (2E)-5-(3-methoxyphenyl)-2-pentenoate (**28b**).* Yield 72% (colorless oil); IR (neat) 1725, 1659, 1603 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.21 (1H, t, *J*=7.8 Hz), 7.00 (1H, dt, *J*=15.8, 6.8 Hz), 6.80–6.70 (3H, m), 5.85 (1H, dt, *J*=15.8, 1.6 Hz), 3.79 (3H, s), 3.71 (3H, s), 2.75 (2H, t, *J*=7.7 Hz), 2.59–2.47 (2H, m); ^{13}C NMR (68 MHz, $CDCl_3$) δ 166.92, 159.68, 148.25, 142.31, 129.40, 121.41, 120.66, 114.11, 111.38, 55.09, 51.37, 34.31, 33.69; EIMS *m*/*z* 220 (M^+), 189, 160, 147, 121, 84; HRMS (EI) *m*/*z* 220.1080 (calcd for $C_{13}H_{16}O_3$: 220.1099).

*5.4.10. Methyl (2E)-5-(3,4-dimethoxyphenyl)-2-pentenoate (**28c**).* Yield 78% (colorless oil); IR (neat) 1721, 1657 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.00 (1H, dt, *J*=15.5, 6.8 Hz), 6.80 (1H, d, *J*=8.2 Hz), 6.75 (1H, dd, *J*=8.2, 2.0 Hz), 6.69 (1H, d, *J*=2.0 Hz), 5.84 (1H, dt, *J*=15.5, 1.6 Hz), 3.87 (3H, s), 3.86 (3H, s), 3.72 (3H, s), 2.73 (2H, t, *J*=6.8 Hz), 2.51 (2H, q, *J*=6.8 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 166.62, 148.59, 148.12, 147.15, 133.05, 121.14, 119.90, 111.42, 111.03, 55.59, 55.51, 51.08, 33.79, 33.64; EIMS *m*/*z* 250 (M^+), 219, 151, 107, 78, HRMS (EI) *m*/*z* 250.1198 (calcd for $C_{14}H_{18}O_4$: 250.1204).

*5.4.11. Methyl (2E)-5-(4-methoxyphenyl)-2-pentenoate (**28d**).* Yield 87% (colorless oil); IR (neat) 1717, 1655, 1615 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (2H, d, *J*=8.3 Hz), 6.99 (1H, dt, *J*=15.6, 6.8 Hz), 6.83 (2H, d, *J*=8.3 Hz), 5.83 (1H, d, *J*=15.6 Hz), 3.79 (3H, s), 3.72 (3H, s), 2.72 (2H, t, *J*=6.8 Hz), 2.49 (2H, q, *J*=6.8 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 166.90, 157.91, 148.41, 132.70, 129.15 (2C), 121.31, 113.79 (2C), 55.13, 51.32, 34.06, 33.35; EIMS *m*/*z* 220 (M^+), 151, 121, 91; HRMS (EI) *m*/*z* 220.1070 (calcd for $C_{13}H_{16}O_3$: 220.1099).

*5.4.12. Ethyl (2E)-5-(3-methoxyphenyl)-2-methyl-2-pentenoate (**31b**).* Yield 91% (colorless oil); IR (neat) 1711, 1653 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.24–7.16 (1H, m), 6.84–6.71 (4H, m), 4.21 (2H, q, *J*=7.3 Hz), 3.80 (3H, s), 2.73 (2H, t, *J*=7.6 Hz), 2.48 (2H, q, *J*=7.6 Hz), 1.79 (3H, d, *J*=1.3 Hz), 1.29 (3H, t, *J*=7.3 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 168.05, 159.63, 142.82, 140.80, 129.35, 128.39, 120.66, 114.08, 111.29, 60.36, 55.07, 34.71, 30.40, 14.22, 12.28; EIMS *m*/*z* 248 (M^+), 202, 174; HRMS (EI) *m*/*z* 248.1382 (calcd for $C_{15}H_{20}O_3$: 248.1412).

5.5. Reduction of arylalkenoates with DIBAL-H

To a solution of **17**, **21**, **28** or **31** in toluene was added dropwise diisobutylaluminium hydride (toluene solution, 2.5 equiv) at −78 °C under an argon atmosphere. The mixture was stirred at −78 °C for 0.5–1 h and then quenched with H_2O. The precipitate was removed by filtration. The filtrate was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluted with hexane/AcOEt (2/1) to give allyl alcohol **18**, **22**, **29** or **32**.

*5.5.1. (2E)-6-(3-Methoxyphenyl)-2-hexen-1-ol (**18b**).* Yield 100% (colorless oil); IR (neat) 3350, 1671 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.19 (1H, dd, *J*=8.9, 7.5 Hz), 6.80–6.70 (3H, m), 5.77–5.58 (2H, m), 4.09 (2H, br), 3.79 (3H, s), 2.60 (2H, t, *J*=7.6 Hz), 2.09 (2H, q, *J*=7.6 Hz), 1.72 (2H, quintet, *J*=7.6 Hz), 1.26 (1H, br); ^{13}C NMR (68 MHz, $CDCl_3$) δ 159.48, 143.85, 132.44, 129.34, 129.10, 120.78, 114.15, 110.86, 63.45, 54.98, 35.26, 31.60, 30.52; EIMS *m*/*z* 206 (M^+), 188, 161, 147, 107; HRMS (EI) *m*/*z* 206.1282 (calcd for $C_{13}H_{18}O_2$: 206.1306).

*5.5.2. (2E)-6-(3,4-Dimethoxyphenyl)-2-hexen-1-ol (**18c**).* Yield 88% (colorless oil); IR (neat) 3398, 1593, 1518 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 6.79 (1H, d, *J*=8.5 Hz), 6.74–6.68 (2H, m), 5.79–5.59 (2H, m), 4.10 (2H, br), 3.87 (3H, s), 3.86 (3H, s), 2.57 (2H, t, *J*=7.6 Hz), 2.09 (2H, q, *J*=7.6 Hz), 1.70 (2H, quintet, *J*=7.6 Hz), 1.30 (1H, br); ^{13}C NMR (68 MHz, $CDCl_3$) δ 148.71, 147.04, 134.91, 132.63, 129.29, 120.13, 111.75, 111.16, 63.58, 55.84, 55.73, 34.85, 31.62, 30.87; EIMS *m*/*z* 236 (M^+), 218, 191, 177; HRMS (EI) *m*/*z* 236.1426 (calcd for $C_{14}H_{20}O_3$: 236.1411).

*5.5.3. (2E)-6-(4-Methoxyphenyl)-2-hexen-1-ol (**18d**).* Yield 99% (colorless oil); IR (neat) 3390, 1667, 1615 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.08 (2H, d, *J*=8.9 Hz), 6.82 (2H, d, *J*=8.9 Hz), 5.77–5.58 (2H, m), 4.09 (2H, t, *J*=5.6 Hz), 3.78 (3H, s), 2.56 (2H, t, *J*=7.9 Hz), 2.08 (2H, q, *J*=7.9 Hz), 1.68 (2H, quintet, *J*=7.9 Hz), 1.22 (1H, t, *J*=5.6 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 157.49, 134.24, 132.40, 129.23, 129.12 (2C), 113.53 (2C), 63.35, 55.03, 34.24, 31.50, 30.85; EIMS *m*/*z* 206 (M^+), 147, 134; HRMS (EI) *m*/*z* 206.1332 (calcd for $C_{13}H_{18}O_2$: 206.1306).

*5.5.4. (2E)-6-(3-Methoxyphenyl)-2-methyl-2-hexen-1-ol (**22b**).* Yield 100% (colorless oil); IR (neat) 3374, 1603 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.24–7.15 (1H, m), 6.82–6.69 (3H, m), 5.43 (1H, tq, *J*=5.8, 1.2 Hz), 4.00 (2H, s), 3.80 (3H, s), 2.60 (2H, t, *J*=7.6 Hz), 2.08 (2H, q, *J*=7.6 Hz), 1.70 (2H, quintet, *J*=7.6 Hz), 1.65 (3H, s), 1.30 (1H, br); ^{13}C NMR (68 MHz, $CDCl_3$) δ 159.60, 144.07, 135.11, 129.18, 125.92, 120.86, 114.22, 110.94, 68.95, 55.13, 35.54, 30.98, 27.18, 13.71; EIMS *m*/*z* 220 (M^+), 202, 192; HRMS (EI) *m*/*z* 220.1489 (calcd for $C_{14}H_{20}O_2$: 220.1462).

*5.5.5. (2E)-6-(3,4-Dimethoxyphenyl)-2-methyl-2-hexen-1-ol (**22c**).* Yield 98% (colorless oil); IR (neat) 3424, 1673, 1593 cm^{-1}; ^{1}H NMR

(400 MHz, $CDCl_3$) δ 6.79 (1H, d, J=8.8 Hz), 6.71 (1H, d, J=8.8 Hz), 6.70 (1H, s), 5.44 (1H, t, J=7.3 Hz), 4.01 (2H, d, J=5.6 Hz), 3.87 (3H, s), 3.86 (3H, s), 2.57 (2H, t, J=7.3 Hz), 2.08 (2H, q, J=7.3 Hz), 1.68 (2H, quintet, J=7.3 Hz), 1.65 (3H, s), 1.28 (1H, t, J=5.6 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 148.68, 146.99, 135.00, 134.96, 125.72, 120.09, 111.69, 111.12, 68.75, 55.82, 55.69, 34.97, 31.22, 27.05, 13.61; EIMS m/z 250 (M^+), 232, 217, 191; HRMS (EI) m/z 250.1538 (calcd for $C_{15}H_{22}O_3$: 250.1568).

*5.5.6. (2E)-6-(4-Methoxyphenyl)-2-methyl-2-hexen-1-ol (**22d**).* Yield 100% (colorless oil); IR (neat) 3386, 1613, 1514 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (2H, d, J=8.8 Hz), 6.82 (2H, d, J=8.8 Hz), 5.43 (1H, tq, J=7.3, 1.5 Hz), 4.01 (2H, d, J=5.3 Hz), 3.79 (3H, s), 2.56 (2H, t, J=7.3 Hz), 2.05 (2H, q, J=7.3 Hz), 1.66 (2H, quintet, J=7.3 Hz), 1.64 (3H, s), 1.24 (1H, t, J=5.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.48, 134.87, 134.37, 129.10 (2C), 125.62, 113.52 (2C), 68.55, 55.04, 34.40, 31.24, 26.96, 13.52; EIMS m/z 220 (M^+), 147, 134; HRMS (EI) m/z 220.1437 (calcd for $C_{14}H_{20}O_2$: 220.1462).

*5.5.7. (2E)-2-Methyl-6-(4-Methylphenyl)-2-hexen-1-ol (**22e**).* Yield 85% (colorless oil); IR (neat) 3332, 1673 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (2H, d, J=9.3 Hz), 7.06 (2H, d, J=9.3 Hz), 5.42 (1H, t, J=7.6 Hz), 4.00 (2H, s), 2.58 (2H, t, J=7.6 Hz), 2.32 (3H, s), 2.07 (2H, q, J=7.6 Hz), 1.68 (2H, quintet, J=7.6 Hz), 1.65 (3H, s), 1.26 (1H, br); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.20, 134.88 (2C), 128.82 (2C), 128.16 (2C), 125.62, 68.48, 34.92, 31.17, 27.06, 20.84, 13.55; EIMS m/z 204 (M^+), 186, 171; HRMS (EI) m/z 204.1521 (calcd for $C_{14}H_{20}O$: 204.1513).

*5.5.8. (2E)-2-Methyl-2-octen-1-ol (**22f**).* Yield 72% (colorless oil); IR (neat) 3318, 1462 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 5.41 (1H, tq, J=7.3, 1.3 Hz), 4.00 (2H, d, J=5.6 Hz), 2.02 (2H, q, J=6.9 Hz), 1.66 (3H, s), 1.44–1.19 (7H, m), 0.89 (3H, t, J=6.9 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 134.52, 126.66, 69.06, 31.53, 29.18, 27.55, 22.56, 14.03, 13.61; EIMS m/z 142 (M^+), 121, 100; HRMS (EI) m/z 142.1362 (calcd for $C_9H_{18}O$: 142.1357).

*5.5.9. (2E)-5-(3-Methoxyphenyl)-2-penten-1-ol (**29b**).* Yield 86% (colorless oil); IR (neat) 3370, 1671, 1603 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.20 (1H, dd, J=8.9, 7.5 Hz), 6.85–6.70 (3H, m), 5.80–5.55 (2H, m), 4.07 (2H, br d, J=4.6 Hz), 3.79 (3H, s), 2.68 (2H, t, J=7.8 Hz), 2.45–2.30 (2H, m), 1.50 (1H, br); ^{13}C NMR (68 MHz, $CDCl_3$) δ 159.57, 143.30, 132.10, 129.61, 129.22, 120.80, 114.24, 111.05, 63.58, 55.09, 35.52, 33.78; EIMS m/z 192 (M^+), 121, 84; HRMS (EI) m/z 192.1158 (calcd for $C_{12}H_{16}O_2$: 192.1149).

*5.5.10. (2E)-5-(3,4-Dimethoxyphenyl)-2-penten-1-ol (**29c**).* Yield 85% (colorless oil); IR (neat) 3496, 1671, 1593, 1516 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 6.82–6.68 (3H, m), 5.80–5.61 (2H, m), 4.09 (2H, t, J=4.8 Hz), 3.87 (3H, s), 3.86 (3H, s), 2.66 (2H, t, J=7.8 Hz), 2.41–2.30 (2H, m), 1.27 (1H, br t, J=4.8 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 148.27, 146.68, 133.99, 131.14, 129.27, 119.76, 111.38, 110.84, 62.74, 55.40, 55.31, 34.67, 33.74; EIMS m/z 222 (M^+), 151, 120, 107, 87, HRMS (EI) m/z 222.1253 (calcd for $C_{13}H_{18}O_3$: 222.1255).

*5.5.11. (2E)-5-(4-Methoxyphenyl)-2-penten-1-ol (**29d**).* Yield 82% (colorless oil); IR (neat) 3350, 1613, 1514 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.09 (2H, d, J=8.6 Hz), 6.83 (2H, d, J=8.6 Hz), 5.79–5.57 (2H, m), 4.08 (2H, t, J=4.9 Hz), 3.79 (3H, s), 2.60 (2H, t, J=8.0 Hz), 2.38–2.29 (2H, m), 1.26 (1H, t, J=4.9 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 157.70, 133.74, 132.22, 129.47, 129.23 (2C), 113.66 (2C), 63.58, 55.18, 34.55, 34.15; EIMS m/z 192 (M^+), 151, 121, 83; HRMS (EI) m/z 192.1177 (calcd for $C_{12}H_{16}O_2$ 192.1149).

*5.5.12. (2E)-5-(3-Methoxyphenyl)-2-methyl-2-penten-1-ol (**32b**).* Yield 76% (colorless oil); IR (neat) 3374, 1603 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.19 (1H, dd, J=8.6, 7.3 Hz), 6.82–6.70 (3H, m), 5.45 (1H, t, J=7.3 Hz), 4.00 (2H, d, J=5.9 Hz), 3.80 (3H, s), 2.65 (2H, t, J=7.3 Hz), 2.36 (2H, q, J=7.3 Hz), 1.63 (3H, s), 1.30 (1H, t, J=5.9 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 159.50, 143.58, 135.43, 129.18, 125.06, 120.79, 114.22, 110.94, 68.70, 55.06, 35.66, 29.31, 13.57; EIMS m/z 206 (M^+), 178, 149; HRMS (EI) m/z 206.1329 (calcd for $C_{13}H_{18}O_2$: 206.1307).

5.6. Epoxidation of aryl-2-alken-1-ol

Epoxidation of **18**, **22**, **29**, and **32** was performed according to that of **15**.

5.6.1. (2R,3R*)-2,3-Epoxy-6-(3-methoxyphenyl)-1-hexanol (**19b**).* Yield 91% (colorless oil); IR (neat) 3420, 1154 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.20 (1H, dd, J=9.1, 7.5 Hz), 6.81–6.71 (3H, m), 3.89 (1H, ddd, J=12.5, 5.5, 2.5 Hz), 3.80 (3H, s), 3.62 (1H, ddd, J=12.5, 7.3, 4.3 Hz), 3.00–2.87 (2H, m), 2.65 (2H, t, J=7.6 Hz), 1.88–1.50 (5H, m); ^{13}C NMR (68 MHz, $CDCl_3$) δ 159.64, 143.49, 129.29, 120.79, 114.20, 111.09, 61.62, 58.33, 55.75, 55.11, 35.52, 31.01, 27.49; EIMS m/z 222 (M^+), 191, 173, 161; HRMS (EI) m/z 222.1282 (calcd for $C_{13}H_{18}O_3$: 222.1255).

5.6.2. (2R,3R*)-2,3-Epoxy-6-(3,4-dimethoxyphenyl)-1-hexanol (**19c**).* Yield 80% (colorless oil); IR (neat) 3442, 1593, 1518 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 6.79 (1H, d, J=8.8 Hz), 6.75–6.69 (2H, m), 3.93 (1H, d, J=2.7 Hz), 3.87 (3H, s), 3.86 (3H, s), 3.62 (1H, dd, J=12.5, 4.2 Hz), 3.02–2.95 (1H, m), 2.94–2.89 (1H, m), 2.62 (2H, t, J=7.5 Hz), 1.90–1.50 (5H, m); ^{13}C NMR (68 MHz, $CDCl_3$) δ 148.69, 147.06, 134.41, 120.05, 111.62, 111.14, 61.60, 58.33, 55.79, 55.68 (2C), 34.96, 30.89, 27.71; EIMS m/z 252 (M^+), 191, 177, 164; HRMS (EI) m/z 252.1371 (calcd for $C_{14}H_{20}O_4$: 252.1360).

5.6.3. (2R,3R*)-2,3-Epoxy-6-(4-methoxyphenyl)-1-hexanol (**19d**).* Yield 86% (colorless oil); IR (neat) 3450, 1613, 1584, 1516 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.09 (2H, d, J=8.6 Hz), 6.82 (2H, d, J=8.6 Hz), 3.89 (1H, ddd, J=12.5, 5.5, 2.5 Hz), 3.79 (3H, s), 3.62 (1H, ddd, J=12.5, 7.3, 4.3 Hz), 2.97 (1H, td, J=5.5, 2.3 Hz), 2.93–2.88 (1H, m), 2.61 (2H, t, J=7.6 Hz), 1.85–1.48 (5H, m); ^{13}C NMR (68 MHz, $CDCl_3$) δ 157.79, 133.92, 129.25 (2C), 113.76 (2C), 61.67, 58.36, 55.79, 55.24, 34.58, 30.98, 27.87; EIMS m/z 222 (M^+), 173, 161, 147, 134, 121, 103, 91; HRMS (EI) m/z 222.1278 (calcd for $C_{13}H_{18}O_3$ 222.1255).

5.6.4. (2R,3R*)-2,3-Epoxy-6-(3-methoxyphenyl)-2-methyl-1-hexanol (**23b**).* Yield 90% (colorless oil); IR (neat) 3426 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.20 (1H, dd, J=8.9, 7.5 Hz), 6.82–6.69 (3H, m), 3.80 (3H, s), 3.72–3.50 (2H, m), 3.06 (1H, t, J=6.1 Hz), 2.73–2.59 (2H, m), 1.94–1.52 (5H, m), 1.26 (3H, s); ^{13}C NMR (68 MHz, $CDCl_3$) δ 159.60, 143.54, 129.31, 120.80, 114.22, 111.16, 65.30, 60.72, 59.93, 55.14, 35.62, 28.10, 27.77, 14.24; EIMS m/z 236 (M^+), 178, 161; HRMS (EI) m/z 236.1434 (calcd for $C_{14}H_{20}O_3$: 236.1411).

5.6.5. (2R,3R*)-2,3-Epoxy-6-(3,4-dimethoxyphenyl)-2-methyl-1-hexanol (**23c**).* Yield 88% (colorless oil); IR (neat) 3472 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.80 (1H, dd, J=6.8, 2.0 Hz), 6.73 (1H, dd, J=6.8, 2.0 Hz), 6.72 (1H, d, J=2.0 Hz), 3.88 (3H, s), 3.86 (3H, s), 3.68 (1H, dd, J=12.2, 4.4 Hz), 3.58 (1H, dd, J=12.2, 8.8 Hz), 3.07 (1H, t, J=6.2 Hz), 2.72–2.57 (2H, m), 1.92–1.68 (5H, m), 1.26 (3H, s); ^{13}C NMR (68 MHz, $CDCl_3$) δ 148.75, 147.14, 134.47, 120.09, 111.66, 111.18, 65.28, 60.75, 59.91, 55.82, 55.73, 35.05, 28.32, 27.60, 14.13; EIMS m/z 266 (M^+), 248, 208; HRMS (EI) m/z 266.1524 (calcd for $C_{15}H_{22}O_4$: 266.1517).

5.6.6. (2R,3R*)-2,3-Epoxy-6-(4-methoxyphenyl)-2-methyl-1-hexanol (**23d**).* Yield 86% (colorless oil); IR (neat) 3428 cm^{-1}; ^{1}H NMR

(400 MHz, $CDCl_3$) δ 7.10 (2H, d, J=8.6 Hz), 6.83 (2H, d, J=8.6 Hz), 3.79 (3H, s), 3.67 (1H, d, J=12.2 Hz), 3.57 (1H, d, J=12.2 Hz), 3.05 (1H, t, J=6.3 Hz), 2.70–2.56 (2H, m), 1.88–1.55 (5H, m), 1.25 (3H, s); ^{13}C NMR (68 MHz, $CDCl_3$) δ 157.53, 133.72, 129.00 (2C), 113.51 (2C), 65.41, 60.91, 60.01, 54.93, 34.37, 28.19, 27.40, 13.88; EIMS m/z 236 (M^+), 178, 161; HRMS (EI) m/z 236.1440 (calcd for $C_{14}H_{20}O_3$: 236.1411).

5.6.7. (2R,3R*)-2,3-Epoxy-2-methyl-6-(4-methylphenyl)-1-hexanol (**23e**).* Yield 100% (colorless oil); IR (neat) 3426 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (2H, d, J=8.6 Hz), 7.07 (2H, d, J=8.6 Hz), 3.67 (1H, d, J=12.2 Hz), 3.56 (1H, d, J=12.2 Hz), 3.05 (1H, t, J=6.1 Hz), 2.72–2.57 (2H, m), 2.32 (3H, s), 1.89–1.53 (5H, m), 1.26 (3H, s); ^{13}C NMR (68 MHz, $CDCl_3$) δ 138.42, 134.76, 128.63 (2C), 127.88 (2C), 65.41, 60.85, 59.95, 34.73, 27.96, 27.35, 20.60, 13.74; EIMS m/z 220 (M^+), 202, 171; HRMS (EI) m/z 220.1457 (calcd for $C_{14}H_{20}O_2$: 220.1462).

5.6.8. (2R,3R*)-2,3-Epoxy-2-methyl-1-octanol (**23f**).* Yield 77% (colorless oil); IR (neat) 3422, 2928 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.69 (1H, dd, J=12.2, 4.6 Hz), 3.58 (1H, dd, J=12.2, 8.6 Hz), 3.04 (1H, t, J=6.1 Hz), 1.72–1.30 (9H, m), 1.28 (3H, s), 0.90 (3H, t, J=7.1 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 65.51, 61.05, 60.33, 31.45, 27.94, 25.95, 22.38, 13.95, 13.77; EIMS m/z 158 (M^+), 139, 83; HRMS (EI) m/z 158.1303 (calcd for $C_9H_{18}O_2$: 158.1306).

5.6.9. (2R,3R*)-2,3-Epoxy-5-(3-methoxylphenyl)-1-pentanol (**30b**).* Yield 91% (colorless oil); IR (neat) 3442, 1603 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.21 (1H, dd, J=8.9, 7.6 Hz), 6.81–6.72 (3H, m), 3.85 (1H, ddd, J=12.5, 5.6, 2.6 Hz), 3.79 (3H, s), 3.57 (1H, ddd, J=12.5, 7.6, 4.3 Hz), 2.99 (1H, td, J=5.6, 2.3 Hz), 2.86 (1H, dt, J=5.6, 2.3 Hz), 2.85–2.64 (2H, m), 1.95–1.84 (2H, m), 1.72–1.61(1H, m); ^{13}C NMR (68 MHz, $CDCl_3$) δ 159.70, 142.64, 129.42, 120.73, 114.19, 111.31, 61.62, 58.61, 55.33, 55.11, 33.20, 32.19; EIMS m/z 208 (M^+), 147, 134, 119, 84; HRMS (EI) m/z 208.1098 (calcd for $C_{12}H_{16}O_3$: 208.1099).

5.6.10. (2R,3R*)-2,3-Epoxy-5-(3,4-dimethoxylphenyl)-1-pentanol (**30c**).* Yield 80% (colorless oil); IR (neat) 3472, 1593, 1518 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 6.80 (1H, d, J=8.2 Hz), 6.73 (1H, dd, J=8.2, 2.0 Hz), 6.71 (1H, d, J=2.0 Hz), 3.91–3.80 (1H, m), 3.87 (3H, s), 3.86 (3H, s), 3.64–3.52 (1H, m), 3.00 (1H, td, J=5.9, 2.3 Hz), 2.90–2.85 (1H, m), 2.84–2.61 (2H, m), 1.93–1.83 (2H, m), 1.69 (1H, br); ^{13}C NMR (68 MHz, $CDCl_3$) δ 148.48, 146.94, 133.36, 119.85, 111.37, 110.98, 61.47, 58.56, 55.53, 55.45, 55.13, 33.21, 31.39; EIMS m/z 238 (M^+), 220, 207, 194, 177, 164, 151, HRMS (EI) m/z 238.1206 (calcd for $C_{13}H_{18}O_4$: 238.1204).

5.6.11. (2R,3R*)-2,3-Epoxy-5-(4-methoxylphenyl)-1-pentanol (**30d**).* Yield 96% (colorless oil); IR (neat) 3420, 1613, 1584, 1516 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.11 (2H, d, J=8.9 Hz), 6.83 (2H, d, J=8.9 Hz), 3.85 (1H, dd, J=12.5, 2.5 Hz), 3.79 (3H, s), 3.57 (1H, dd, J=12.5, 4.0 Hz), 2.98 (1H, td, J=4.0, 2.5 Hz), 2.90–2.82 (1H, m), 2.82–2.60 (2H, m), 2.00–1.75 (2H, m), 1.66 (1H, br); ^{13}C NMR (68 MHz, $CDCl_3$) δ 157.83, 133.01, 129.18 (2C), 113.77 (2C), 61.64, 58.71, 55.34, 55.14, 33.47, 31.16; EIMS m/z 208 (M^+), 159, 147, 134, 121; HRMS (EI) m/z 208.1123 (calcd for $C_{12}H_{16}O_2$: 208.1099).

5.6.12. (2R,3R*)-2,3-Epoxy-5-(3-methoxylphenyl)-2-methyl-1-pentanol (**33b**).* Yield 82% (colorless oil); IR (neat) 3446, 1603 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.21 (1H, dd, J=8.9, 7.6 Hz), 6.84–6.72 (3H, m), 3.80 (3H, s), 3.64 (1H, dd, J=12.2, 4.5 Hz), 3.53 (1H, dd, J=12.2, 8.6 Hz), 3.09 (1H, t, J=6.3 Hz), 2.90–2.64 (2H, m), 2.03–1.77 (2H, m), 1.66 (1H, dd, J=8.6, 4.5 Hz), 1.15 (3H, s); ^{13}C NMR (68 MHz, $CDCl_3$) δ 159.62, 142.69, 129.36, 120.74, 114.20, 111.26, 65.30, 61.21, 59.57, 55.07, 32.65, 29.89, 14.02; EIMS m/z 222 (M^+), 204, 191; HRMS (EI) m/z 222.1267 (calcd for $C_{13}H_{18}O_3$: 222.1256).

5.7. (3*R**,4*R**)-3,4-Epoxy-7-(3-Methoxyphenyl)-1-heptene (20b)

To a solution of **19b** (422 mg, 1.90 mmol) in CH_2Cl_2 (70 ml) was added Dess–Martin periodinane (1.61 g, 3.80 mmol) at 0 °C under an argon atmosphere. The mixture was stirred at room temperature for 1 h and then quenched with saturated aqueous $NaHCO_3$ and extracted with Et_2O. The extract was washed with saturated aqueous $NaHCO_3$ and NaCl, dried over $MgSO_4$, and concentrated under reduced pressure to give aldehyde. To a suspension of methyltriphenylphosphonium bromide (1.32 g, 2.85 mmol) in THF (10 ml) was added dropwise potassium bis(trimethylsilyl)amide (0.5 M in toluene 4.9 ml, 2.47 mmol) at 0 °C under an argon atmosphere. After being stirred for 30 min, a solution of the aldehyde in THF (10 ml) was added to the mixture at −20 °C. After being stirred for 1 h at −20 °C, the reaction was quenched with H_2O at 0 °C and extracted with Et_2O. The extract was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluted with hexane/AcOEt (10/1) to give **20b** (361 mg, 1.66 mmol, 89%) as a colorless oil: IR (neat) 1603, 1586 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.19 (1H, t, J=7.6 Hz), 6.82–6.67 (3H, m), 5.57 (1H, ddd, J=17.1, 9.9, 7.3 Hz), 5.44 (1H, dd, J=17.1, 2.0 Hz), 5.25 (1H, dd, J=9.9, 1.6 Hz), 3.80 (3H, s), 3.09 (1H, dd, J=7.2, 2.0 Hz), 2.89–2.79 (1H, m), 2.65 (2H, t, J=7.6 Hz), 1.92–1.46 (4H, m); ^{13}C NMR (68 MHz, $CDCl_3$) δ 159.55, 143.41, 135.72, 129.17, 120.68, 118.78, 114.08, 110.99, 60.05, 58.41, 54.94, 35.44, 31.30, 27.38; EIMS m/z 218 (M^+), 200, 177, 161; HRMS (EI) m/z 218.1331 (calcd for $C_{14}H_{18}O_2$: 218.1306).

5.8. Preparation of 16b–d, 24b–f, 27b–d, and 34b

Dess–Martin oxidation of **19**, **23**, **30**, and **33** was carried out according to that of **19b** (see Section 5.7). Wittig reaction of the aldehydes obtained by the oxidation was carried out according to that of **14b–d**.

5.8.1. Methyl (4R,5R*,2E)-4,5-epoxy-8-(3-methoxyphenyl)-2-octenoate (**16b**).* Yield 77% (colorless oil); IR (neat) 1725, 1661 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.20 (1H, td, J=7.6, 1.4 Hz), 6.80–6.70 (3H, m), 6.67 (1H, dd, J=15.6, 7.0 Hz), 6.12 (1H, d, J=15.6 Hz), 3.80 (3H, s), 3.74 (3H, s), 3.19 (1H, dd, J=7.0, 1.9 Hz), 2.89 (1H, td, J=6.5, 1.9 Hz), 2.64 (2H, t, J=7.4 Hz), 1.88–1.57 (4H, m); ^{13}C NMR (68 MHz, $CDCl_3$) δ 166.09, 159.68, 144.95, 143.27, 129.35, 123.13, 120.79, 114.24, 111.14, 61.25, 56.15, 55.13, 51.70, 35.45, 31.33, 27.33; EIMS m/z 276 (M^+), 199, 177, 161; HRMS (EI) m/z 276.1390 (calcd for $C_{16}H_{20}O_4$: 276.1360).

5.8.2. Methyl (4R,5R*,2E)-4,5-epoxy-8-(3,4-dimethoxyphenyl)-2-octenoate (**16c**).* Yield 82% (colorless oil); IR (neat) 1723, 1659 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 6.79 (1H, d, J=8.5 Hz), 6.75–6.63 (3H, m), 6.12 (1H, d, J=15.6 Hz), 3.87 (3H, s), 3.86 (3H, s), 3.74 (3H, s), 3.20 (1H, dd, J=7.0, 1.6 Hz), 2.90 (1H, ddd, J=6.4, 4.9, 1.6 Hz), 2.62 (2H, t, J=7.5 Hz), 1.90–1.52 (4H, m); ^{13}C NMR (68 MHz, $CDCl_3$) δ 165.94, 148.72, 147.13, 144.85, 134.17, 122.98, 120.05, 111.55, 111.11, 61.14, 56.03, 55.77, 55.68, 51.56, 34.90, 31.20, 27.54; EIMS m/z 306 (M^+), 274, 191; HRMS (EI) m/z 306.1487 (calcd for $C_{17}H_{22}O_5$: 306.1466).

5.8.3. Methyl (4R,5R*,2E)-4,5-epoxy-8-(4-methoxyphenyl)-2-octenoate (**16d**).* Yield 63% (colorless oil); IR (neat) 1734, 1661, 1613 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.08 (2H, d, J=8.4 Hz), 6.82 (2H, d, J=8.4 Hz), 6.67 (1H, dd, J=15.5, 6.9 Hz), 6.11 (1H, d, J=15.5 Hz), 3.78 (3H, s), 3.74 (3H, s), 3.19 (1H, dd, J=6.9, 1.6 Hz), 2.89 (1H, td, J=5.4, 1.6 Hz), 2.68 (2H, t, J=7.4 Hz), 1.88–1.50 (4H, m); ^{13}C NMR (68 MHz, $CDCl_3$) δ 166.06, 157.81, 144.97, 133.66, 129.21 (2C),

123.05, 113.75 (2C), 61.26, 56.14, 55.19, 51.66, 34.46, 31.24, 27.63; EIMS *m*/*z* 276 (M^+), 199, 177, 162; HRMS (EI) *m*/*z* 276.1337 (calcd for $C_{16}H_{20}O_4$: 276.1360).

5.8.4. Methyl (4R,5R*,2E)-4,5-epoxy-8-(3-methoxyphenyl)-4-methyl-2-octenoate (**24b**).* Yield 69% (colorless oil); IR (neat) 1723, 1655, 1603 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 7.20 (1H, dd, *J*=8.9, 7.4 Hz), 6.80–6.71 (3H, m), 6.75 (1H, d, *J*=15.8 Hz), 6.00 (1H, d, *J*=15.8 Hz), 3.79 (3H, s), 3.73 (3H, s), 2.85 (1H, t, *J*=6.1 Hz), 2.75–2.56 (2H, m), 1.94–1.52 (4H, m), 1.40 (3H, s); ^{13}C NMR (68 MHz, $CDCl_3$) δ 166.53, 159.68, 150.12, 143.28, 129.33, 121.01, 120.77, 114.20, 111.18, 65.72, 58.37, 55.13, 51.64, 35.51, 28.04, 27.90, 15.17; EIMS *m*/*z* 290 (M^+), 231, 177; HRMS (EI) *m*/*z* 290.1506 (calcd for $C_{17}H_{22}O_4$: 290.1517).

5.8.5. Methyl (4R,5R*,2E)-4,5-epoxy-8-(3,4-dimethoxyphenyl)-4-methyl-2-octenoate (**24c**).* Yield 77% (colorless oil); IR (neat) 1725, 1657, 1607 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.81–6.71 (3H, m), 6.77 (1H, d, *J*=15.7 Hz), 6.02 (1H, d, *J*=15.7 Hz), 3.87 (3H, s), 3.86 (3H, s), 3.74 (3H, s), 2.86 (1H, t, *J*=6.0 Hz), 2.70–2.56 (2H, m), 1.90–1.60 (4H, m), 1.41 (3H, s); ^{13}C NMR (68 MHz, $CDCl_3$) δ 166.50, 150.08, 148.82, 147.25, 134.28, 120.95, 120.14, 111.67, 111.23, 65.71, 58.33, 55.88, 55.79, 51.61, 35.01, 28.17, 27.95, 15.13; EIMS *m*/*z* 320 (M^+), 191, 177; HRMS (EI) *m*/*z* 320.1622 (calcd for $C_{18}H_{24}O_5$: 320.1634).

5.8.6. Methyl (4R,5R*,2E)-4,5-epoxy-8-(4-methoxyphenyl)-4-methyl-2-octenoate (**24d**).* Yield 88% (colorless oil); IR (neat) 1714, 1653, 1613 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.09 (2H, d, *J*=8.3 Hz), 6.83 (2H, d, *J*=8.3 Hz), 6.75 (1H, d, *J*=15.6 Hz), 6.00 (1H, d, *J*=15.6 Hz), 3.79 (3H, s), 3.74 (3H, s), 2.85 (1H, t, *J*=6.1 Hz), 2.70–2.55 (2H, m), 1.89–1.59 (4H, m), 1.40 (3H, s); ^{13}C NMR (68 MHz, $CDCl_3$) δ 166.51, 157.80, 150.15, 133.67, 129.19 (2C), 120.93, 113.74 (2C), 65.72, 58.34, 55.17, 51.61, 34.50, 28.19, 27.92, 15.10; EIMS *m*/*z* 290 (M^+), 177, 162; HRMS (EI) *m*/*z* 290.1536 (calcd for $C_{17}H_{22}O_4$: 290.1517).

5.8.7. Methyl (4R,5R*,2E)-4,5-epoxy-4-methyl-8-(4-methylphenyl)-2-octenoate (**24e**).* Yield 72% (colorless oil); IR (neat) 1723, 1657 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.10 (2H, d, *J*=8.1 Hz), 7.07 (2H, d, *J*=8.1 Hz), 6.75 (1H, d, *J*=15.6 Hz), 6.01 (1H, d, *J*=15.8 Hz), 3.74 (3H, s), 2.85 (1H, t, *J*=5.9 Hz), 2.71–2.56 (2H, m), 2.32 (3H, s), 1.90–1.54 (4H, m), 1.40 (3H, s); ^{13}C NMR (68 MHz, $CDCl_3$) δ 166.36, 150.07, 138.42, 135.18, 128.91 (2C), 128.09 (2C), 120.82, 65.61, 58.21, 51.47, 34.89, 27.97, 27.89, 20.83, 15.01; EIMS *m*/*z* 274 (M^+), 242, 215; HRMS (EI) *m*/*z* 274.1576 (calcd for $C_{17}H_{22}O_4$: 274.1568).

5.8.8. Methyl (4R,5R*,2E)-4,5-epoxy-4-methyl-2-decenoate (**24f**)* Yield 57% (colorless oil); IR (neat) 1725, 1657 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 6.77 (1H, dd, *J*=15.7 Hz), 6.02 (1H, d, *J*=15.7 Hz), 3.74 (3H, s), 2.84 (1H, t, *J*=6.0 Hz), 1.70–1.24 (8H, m), 1.43 (3H, s), 0.90 (3H, t, *J*=6.9 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 166.39, 150.21, 120.72, 65.84, 58.22, 51.45, 31.40, 28.32, 25.84, 22.38, 15.01, 13.78; EIMS *m*/*z* 212 (M^+), 181, 154; HRMS (EI) *m*/*z* 212.1402 (calcd for $C_{12}H_{20}O_3$: 212.1411).

5.8.9. Methyl (4R,5R*,2E)-4,5-epoxy-7-(3-methoxyphenyl)-2-heptenoate (**27b**).* Yield 64% (colorless oil); IR (neat) 1717, 1661 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 7.21 (1H, t, *J*=7.7 Hz), 6.79–6.73 (3H, m), 6.63 (1H, dd, *J*=15.6, 7.0 Hz), 6.05 (1H, d, *J*=15.6 Hz), 3.79 (3H, s), 3.74 (3H, s), 3.13 (1H, dd, *J*=7.0, 2.0 Hz), 2.91 (1H, td, *J*=5.7, 2.0 Hz), 2.88–2.64 (2H, m), 2.05–1.80 (2H, m); ^{13}C NMR (68 MHz, $CDCl_3$) δ 166.06, 159.77, 144.81, 142.37, 129.50, 123.19, 120.73, 114.24, 111.40, 60.66, 56.46, 55.13, 51.68, 33.58, 32.06; EIMS *m*/*z* 262 (M^+), 244, 148; HRMS (EI) *m*/*z* 262.1178 (calcd for $C_{15}H_{18}O_4$: 262.1204).

5.8.10. Methyl (4R,5R*,2E)-4,5-epoxy-7-(3,4-dimethoxyphenyl)-2-heptenoate (**27c**).* Yield 40% (colorless oil); IR ($CHCl_3$) 1729, 1661 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 6.80 (1H, d, *J*=8.1 Hz), 6.74–6.70 (2H, m), 6.65 (1H, dd, *J*=15.5, 7.0 Hz), 6.07 (1H, d, *J*=15.5 Hz), 3.86 (6H, s), 3.74 (3H, s), 3.16 (1H, dd, *J*=7.0, 1.9 Hz), 2.91 (1H, td, *J*=5.7, 1.9 Hz), 2.85–2.62 (2H, m), 1.97–1.86 (2H, m); ^{13}C NMR (68 MHz, $CDCl_3$) δ 166.02, 148.95, 147.45, 144.81, 133.33, 123.15, 120.20, 111.64, 111.33, 60.72, 56.40, 55.91, 55.80, 51.66, 33.85, 31.62; EIMS *m*/*z* 292 (M^+), 164, 151; HRMS (EI) *m*/*z* 292.1325 (calcd for $C_{16}H_{20}O_5$: 292.1310).

5.8.11. Methyl (4R,5R*,2E)-4,5-epoxy-7-(4-methoxyphenyl)-2-heptenoate (**27d**).* Yield 89% (white needles); mp 59 °C (hexane/toluene=10/1). Anal. Calcd for $C_{15}H_{18}O_4$: C, 68.69; H, 6.92. Found: C, 68.58; H, 6.93. IR (neat) 1717, 1661 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 7.10 (2H, d, *J*=8.6 Hz), 6.83 (2H, d, *J*=8.6 Hz), 6.64 (1H, dd, *J*=15.8, 7.0 Hz), 6.06 (1H, d, *J*=15.8 Hz), 3.79 (3H, s), 3.74 (3H, s), 3.13 (1H, dd, *J*=7.0, 1.5 Hz), 2.90 (1H, td, *J*=5.7, 1.5 Hz), 2.84–2.66 (2H, m), 2.00–1.77 (2H, m); ^{13}C NMR (68 MHz, $CDCl_3$) δ 165.95, 157.89, 144.80, 132.66, 129.16 (2C), 122.99, 113.80 (2C), 60.62, 56.30, 55.10, 51.56, 33.78, 30.99; EIMS *m*/*z* 262 (M^+), 244, 148; HRMS (EI) *m*/*z* 262.1177 (calcd for $C_{15}H_{18}O_4$: 262.1204).

5.8.12. Methyl (4R,5R*,2E)-4,5-epoxy-7-(3-methoxyphenyl)-4-methyl-2-heptenoate (**34b**).* Yield 90% (colorless oil); IR (neat) 1729, 1653 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 7.21 (1H, t, *J*=7.7 Hz), 6.78–6.71 (3H, m), 6.72 (1H, d, *J*=15.5 Hz), 5.96 (1H, d, *J*=15.5 Hz), 3.79 (3H, s), 3.74 (3H, s), 2.88 (1H, t, *J*=6.3 Hz), 2.84–2.62 (2H, m), 2.06–1.78 (2H, m), 1.28 (3H, s); ^{13}C NMR (68 MHz, $CDCl_3$) δ 166.46, 159.64, 149.98, 142.35, 129.42, 121.00, 120.73, 114.18, 111.37, 65.15, 58.71, 55.04, 51.60, 32.46, 30.22, 14.96; EIMS *m*/*z* 276 (M^+), 217, 147, 83; HRMS (EI) *m*/*z* 276.1336 (calcd for $C_{16}H_{20}O_4$: 276.1360).

5.9. $BF_3 \cdot Et_2O$-promoted reaction of vinyloxiranes 16, 20, 24, 27 or 34

As a representative example, the reaction of **16b** was performed in the following manner. To a solution of **16b** (150 mg, 0.543 mmol) in CH_2Cl_2 (20 ml) was added $BF_3 \cdot Et_2O$ (34 μl, 0.269 mmol) at −30 °C under an argon atmosphere. The mixture was stirred at −30 °C for 10 min, then quenched with saturated aqueous $NaHCO_3$ and extracted with Et_2O. The extract was washed with saturated aqueous NaCl, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give **36b** (145 mg, 0.525 mmol, 97%). Spectroscopic data are shown in Section 5.9.3.

*5.9.1. 5-Ethenyl-6,7,8,9-tetrahydro-2-methoxy-5H-benzocyclohepten-6-ol (**35b**).* Cyclized product **35b** was obtained in 85% yield as as epimeric mixture with a ratio of 1.6/1. A part of the epimers was separated by flash column chromatography. For less polar: IR (neat) 3404, 1609 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 7.09 (1H, d, *J*=7.8 Hz), 6.72–6.64 (2H, m), 6.31 (1H, ddd, *J*=17.3, 10.5, 6.8 Hz), 5.21 (1H, dt, *J*=10.5, 1.5 Hz), 5.03 (1H, dt, *J*=17.3, 1.5 Hz), 3.98–3.88 (1H, m), 3.78 (3H, s), 3.71 (1H, d, *J*=7.1 Hz), 2.84 (1H, dd, *J*=12.7, 10.5 Hz), 2.66 (1H, dd, *J*=12.7, 7.8 Hz), 2.10–1.75 (2H, m), 1.74–1.51 (2H, m), 1.44 (1H, d, *J*=7.1 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 158.39, 144.24, 136.90, 131.75, 130.17, 116.70, 116.17, 110.79, 72.03, 55.88, 55.16, 36.75, 35.82, 24.78; EIMS *m*/*z* 218 (M^+), 174, 161; HRMS (EI) *m*/*z* 218.1279 (calcd for $C_{14}H_{18}O_2$: 218.1306). For more polar: IR (neat) 3422, 1609 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.08 (1H, d, *J*=7.8 Hz), 6.73–6.64 (2H, m), 6.09 (1H, ddd, *J*=17.1, 10.3, 6.3 Hz), 5.18 (1H, d, *J*=10.3 Hz), 4.94 (1H, d, *J*=17.1 Hz), 4.01 (1H, br), 3.79 (3H, s), 3.72 (1H, t, *J*=6.3 Hz), 2.92–2.81 (1H, m), 2.71–2.61 (1H, m), 2.05–1.85 (2H, m), 1.80–1.63 (2H, m), 1.51 (1H, d, *J*=7.3 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 158.60, 144.15, 137.41, 132.48, 129.46, 116.52, 116.20, 110.72, 71.12, 56.54, 55.12, 35.68, 34.44, 22.01; EIMS *m*/*z* 218

(M^+), 174, 166, 147; HRMS (EI) *m/z* 218.1290 (calcd for $C_{14}H_{18}O_2$: 218.1306).

5.9.2. (5R,6R*)-5-(Methoxycarbonyl-(E)-ethenyl)-6,7,8,9-tetrahydro-5H-benzocyclohepten-6-ol (**36a**).* Yield 25% (colorless oil); IR (neat) 3454, 1723, 1653 cm^{-1}; ^1H NMR (270 MHz, C_6D_6) δ 7.27 (1H, dd, *J*=15.8, 6.3 Hz), 7.04–6.83 (4H, m), 5.68 (1H, dd, *J*=15.8, 1.8 Hz), 3.74 (1H, br), 3.53 (1H, td, *J*=6.3, 1.8 Hz), 3.38 (3H, s), 2.61–2.48 (1H, m), 2.41–2.29 (1H, m), 1.70–1.42 (3H, m), 1.40–1.22 (1H, m), 0.98 (1H, br); ^{13}C NMR (68 MHz, $CDCl_3$) δ 166.80, 147.45, 142.45, 135.96, 131.87, 130.38, 127.79, 126.61, 122.06, 70.58, 56.05, 51.51, 35.51, 34.79, 21.59. EIMS *m/z* 246 (M^+), 214, 186, 170, 157, 128, 115; HRMS (EI) *m/z* 246.1242 (calcd for $C_{15}H_{18}O_3$: 246.1255).

5.9.3. (5R,6R*)-2-Methoxy-5-(methoxycarbonyl-(E)-ethenyl)-6,7,8,9-tetrahydro-5H-benzocyclohepten-6-ol (**36b**).* Yield 97% (colorless oil); IR (neat) 3462, 1721, 1649 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 7.20 (1H, dd, *J*=15.6, 5.9 Hz), 7.04 (1H, d, *J*=9.3 Hz), 6.73–6.67 (2H, m), 5.60 (1H, dd, *J*=15.6, 2.0 Hz), 4.20 (1H, br), 3.88 (1H, td, *J*=5.9, 2.0 Hz), 3.79 (3H, s), 3.71 (3H, s), 2.79 (1H, ddd, *J*=14.1, 9.3, 3.4 Hz), 2.64 (1H, ddd, *J*=14.1, 5.9, 2.4 Hz), 2.04–1.87 (2H, m), 1.77–1.64 (2H, m), 1.58 (1H, br); ^{13}C NMR (68 MHz, $CDCl_3$) δ 166.86, 159.09, 147.80, 144.07, 133.33, 127.57, 122.00, 116.59, 111.07, 70.55, 55.40, 55.18, 51.51, 35.84, 34.70, 21.63; EIMS *m/z* 276 (M^+), 258, 244, 216; HRMS (EI) *m/z* 276.1386 (calcd for $C_{16}H_{20}O_4$: 276.1360).

5.9.4. (5R,6R*)-2,3-Dimethoxy-5-(methoxycarbonyl-(E)-ethenyl)-6,7,8,9-tetrahydro-5H-benzocyclohepten-6-ol (**36c**).* Yield 95% (white needles); mp 144 °C (toluene). Anal. Calcd for $C_{17}H_{22}O_5$: C, 66.65; H, 7.24. Found: C, 66.71; H, 7.37. IR (neat) 3498, 1717, 1653 cm^{-1}; ^1H NMR (270 MHz, C_6D_6) δ 7.30 (1H, dd, *J*=15.8, 5.6 Hz), 6.47 (1H, s), 6.40 (1H, s), 5.77 (1H, dd, *J*=15.8, 2.0 Hz), 3.87 (1H, q, *J*=5.6 Hz), 3.52 (1H, td, *J*=5.6, 2.0 Hz), 3.42 (3H, s), 3.40 (6H, s), 2.58 (1H, dd, *J*=14.5, 10.2 Hz), 2.27 (1H, dd, *J*=14.5, 5.6 Hz), 1.82–1.30 (4H, m), 1.16 (1H, d, *J*=7.5 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 166.82, 147.79, 147.40, 147.01, 134.93, 127.34, 121.91, 115.85, 114.13, 70.43, 55.94 (2C), 55.84, 51.47, 35.25, 34.48, 21.59; EIMS *m/z* 306 (M^+), 288, 274; HRMS (EI) *m/z* 306.1445 (calcd for $C_{17}H_{22}O_5$: 306.1466).

5.9.5. (1′R,2′R*)-3-(2′-Hydroxy-9′-oxospiro[5.5]undeca-7′,10′-dien-1′-yl)-2E-propenoic acid methyl ester (**37d**).* Yield 70% (white needles); mp 146–147 °C (toluene). Anal. Calcd for $C_{15}H_{18}O_4$: C, 68.69; H, 6.92. Found: C, 68.97; H, 7.02. IR ($CHCl_3$) 3452, 3024, 1721, 1665 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 7.16 (1H, dd, *J*=10.6, 3.0 Hz), 6.61 (1H, dd, *J*=10.2, 3.0 Hz), 6.46 (1H, dd, *J*=15.6, 9.9 Hz), 6.42 (1H, dd, *J*=10.5, 2.0 Hz), 6.23 (1H, dd, *J*=9.9, 2.0 Hz), 5.87 (1H, d, *J*=15.6 Hz), 3.87 (1H, td, *J*=10.5, 4.6 Hz), 3.69 (3H, s), 2.31–2.20 (2H, m), 1.97–1.38 (6H, m); ^{13}C NMR (68 MHz, $CDCl_3$) δ 185.62, 165.82, 155.22, 148.32, 144.43, 131.08, 128.98, 125.43, 68.07, 55.40, 51.55, 45.79, 35.90, 33.91, 20.54; EIMS *m/z* 262 (M^+), 244, 230; HRMS (EI) *m/z* 262.1216 (calcd for $C_{15}H_{18}O_4$: 262.1204).

*5.9.6. 3-(2,11-Epoxy-9-oxospiro[5.5]undeca-7-en-1-yl)-2E-propenoic acid methyl ester (**38d**).* Yield 9% (colorless oil); IR (neat) 1717, 1620 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 7.16 (1H, dd, *J*=15.5, 9.4 Hz), 6.45 (1H, d, *J*=10.1 Hz), 6.00 (1H, d, *J*=15.5 Hz), 5.96 (1H, d, *J*=10.1 Hz), 4.50 (1H, dd, *J*=10.9, 6.9 Hz), 4.46 (1H, m), 3.78 (3H, s), 3.13 (1H, dd, *J*=9.4, 5.6 Hz), 2.89 (1H, dd, *J*=16.2, 6.9 Hz), 2.55 (1H, dd, *J*=16.2, 10.9 Hz), 2.02–1.70 (5H, m), 1.41 (1H, br d, *J*=7.3 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 197.29, 166.01, 149.73, 141.89, 128.39, 125.61, 80.15, 80.12, 51.75, 49.87, 47.29, 43.92, 30.16, 25.38, 17.44; EIMS *m/z* 262 (M^+), 230, 217; HRMS (EI) *m/z* 262.1227 (calcd for $C_{15}H_{18}O_4$: 262.1204).

5.9.7. (5R,6R*)-2-Methoxy-5-(methoxycarbonyl-(E)-ethenyl)-5-methyl-6,7,8,9-tetrahydro-5H-benzocyclohepten-6-ol (**39b**).* Yield 44% (colorless oil); IR (neat) 3506, 1717 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 7.29 (1H, d, *J*=8.7 Hz), 7.21 (1H, d, *J*=15.9 Hz), 6.74 (1H, dd, *J*=8.7, 2.9 Hz), 6.69 (1H, d, *J*=2.9 Hz), 5.41 (1H, d, *J*=15.9 Hz), 3.98–3.87 (1H, m), 3.80 (3H, s), 3.70 (3H, s), 2.88 (1H, t, *J*=12.3 Hz), 2.59 (1H, dd, *J*=14.0, 5.7 Hz), 2.08–2.00 (2H, m), 1.78–1.45 (2H, m), 1.61 (3H, s), 1.20 (1H, br d, *J*=9.0 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 166.27, 158.72, 154.49, 144.82, 131.24, 130.05, 118.99, 117.39, 110.68, 75.39, 55.13, 51.48, 51.33, 37.07, 35.08, 27.79, 21.46; EIMS *m/z* 290 (M^+), 258, 187; HRMS (EI) *m/z* 290.1490 (calcd for $C_{17}H_{22}O_4$: 290.1517).

5.9.8. (5R,6R*)-4-Methoxy-5-(methoxycarbonyl-(E)-ethenyl)-5-methyl-6,7,8,9-tetrahydro-5H-benzocyclohepten-6-ol (**40b**).* Yield 4% (colorless oil); ^1H NMR (270 MHz, $CDCl_3$) δ 7.28 (1H, d, *J*=16.1 Hz), 7.07 (1H, t, *J*=7.8 Hz), 6.76–6.67 (2H, m), 5.66 (1H, d, *J*=16.1 Hz), 4.24 (1H, m), 3.72 (3H, s), 3.66 (3H, s), 3.11 (1H, dd, *J*=15.4, 12.5 Hz), 2.71 (1H, dd, *J*=15.4, 7.0 Hz), 2.20–1.49 (5H, m), 1.60 (3H, s); EIMS *m/z* 290 (M^+), 258, 187, 83; HRMS (EI) *m/z* 290.1491 (calcd for $C_{17}H_{22}O_4$: 290.1517).

*5.9.9. Methyl (2E)-4-fluoro-5-hydroxy-8-(3-methoxyphenyl)-4-methyl-2-octenoate (**41b**).* Yield 36% (colorless oil); IR (neat) 3482, 1717 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 7.19 (1H, dd, *J*=8.5, 7.6 Hz), 6.93 (1H, dd, *J*=21.1, 15.7 Hz), 6.79–6.70 (3H, m), 6.11 (1H, d, *J*=15.7 Hz), 3.79 (3H, s), 3.76 (3H, s), 3.65 (1H, tdd, *J*=10.7, 8.3, 2.5 Hz), 2.69–2.52 (2H, m), 2.04–1.83 (2H, m), 1.80–1.29 (3H, m), 1.45 (3H, d, *J*=22.5 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 166.67, 159.96, 146.82 (d, *J*=19.9 Hz), 143.94, 129.58, 121.29 (d, *J*=9.9 Hz), 121.07, 114.42, 111.45, 97.90 (d, *J*=175.6 Hz), 76.04 (d, *J*=24.9 Hz), 55.41, 52.07, 35.96, 31.02 (d, *J*=3.7 Hz), 28.11, 20.55 (d, *J*=23.7 Hz); EIMS *m/z* 310 (M^+), 179, 161; HRMS (EI) *m/z* 310.1570 (calcd for $C_{17}H_{23}O_4F$: 310.1579).

*5.9.10. Methyl (2E)-4-formyl-7-(3-methoxyphenyl)-4-methyl-2-heptenoate (**42b**).* Yield 4% (colorless oil); IR (neat) 1725, 1653, 1603 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 9.42 (1H, s), 7.20 (1H, t, *J*=7.9 Hz), 6.96 (1H, d, *J*=16.1 Hz), 6.80–6.67 (3H, m), 5.85 (1H, d, *J*=16.1 Hz), 3.80 (3H, s), 3.75 (3H, s), 2.59 (2H, t, *J*=7.4 Hz), 1.76–1.45 (4H, m), 1.23 (3H, s); ^{13}C NMR (68 MHz, $CDCl_3$) δ 200.85, 166.32, 159.74, 148.10, 143.06, 129.41, 122.21, 120.76, 114.23, 111.24, 55.17, 52.53, 51.74, 36.12, 35.17, 25.63, 18.06; EIMS *m/z* 290 (M^+), 262, 230; HRMS (EI) *m/z* 290.1507 (calcd for $C_{17}H_{22}O_4$: 290.1517).

*5.9.11. Methyl (3E)-8-(3-methoxyphenyl)-4-methyl-5-oxooct-3-enoate (**43b**).* Yield 7% (colorless oil); IR (neat) 1742, 1671 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 7.20 (1H, dd, *J*=8.8, 7.6 Hz), 6.82–6.69 (4H, m), 3.80 (3H, s), 3.74 (3H, s), 3.28 (2H, d, *J*=6.8 Hz), 2.72 (2H, t, *J*=7.3 Hz), 2.62 (2H, t, *J*=7.3 Hz), 1.95 (2H, quintet, *J*=7.3 Hz), 1.78 (3H, s); ^{13}C NMR (68 MHz, $CDCl_3$) δ 201.59, 171.39, 160.14, 143.87, 139.97, 132.92, 129.75, 121.35, 114.61, 111.75, 55.58, 52.61, 36.99, 35.74, 34.63, 26.41, 12.20; EIMS *m/z* 290 (M^+), 259, 217; HRMS (EI) *m/z* 290.1499 (calcd for $C_{17}H_{22}O_4$: 290.1517).

5.9.12. (5R,6R*)-2,3-Dimethoxy-5-(methoxycarbonyl-(E)-ethenyl)-5-methyl-6,7,8,9-tetrahydro-5H-benzocyclohepten-6-ol (**39c**).* Yield 87% (colorless oil); IR (neat) 3512, 1715, 1647 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.20 (1H, d, *J*=16.1 Hz), 6.91 (1H, s), 6.65 (1H, s), 5.42 (1H, d, *J*=16.1 Hz), 3.93 (1H, dt, *J*=9.8, 3.9 Hz), 3.88 (6H, s), 3.71 (3H, s), 2.85 (1H, dd, *J*=14.7, 12.7 Hz), 2.56 (1H, dd, *J*=14.7, 5.9 Hz), 2.08–2.01 (2H, m), 1.74–1.54 (2H, m), 1.63 (3H, s), 1.22 (1H, d, *J*=9.8 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 167.28, 154.11, 147.61, 146.74, 136.05, 129.98, 119.07, 114.91, 114.29, 75.46, 56.12, 55.82, 51.61, 51.53, 36.48, 35.10, 27.88, 21.56; EIMS *m/z* 320 (M^+), 288, 249, 231; HRMS (EI) *m/z* 320.1640 (calcd for $C_{18}H_{24}O_5$: 320.1622).

*5.9.13. Methyl (2E)-4-fluoro-5-hydroxy-8-(4-methoxyphenyl)-4-methyl-2-octenoate (**41d**).* Yield 9% (colorless oil); IR (neat) 3492, 1729 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.08 (2H, d, *J*=8.3 Hz), 6.93

(1H, dd, *J*=21.5, 16.1 Hz), 6.82 (2H, d, *J*=8.3 Hz), 6.10 (1H, d, *J*=16.1 Hz), 3.78 (3H, s), 3.76 (3H, s), 3.64 (1H, t, *J*=9.2 Hz), 2.66–2.48 (2H, m), 2.03 (1H, br), 1.96–1.80 (1H, m), 1.70–1.29 (3H, m), 1.44 (3H, d, *J*=22.4 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 166.42, 157.79, 146.60 (d, *J*=20.1 Hz), 134.10, 129.24 (2C), 120.98 (d, *J*=10.9 Hz), 113.80 (2C), 97.60 (1H, d, *J*=175.6), 75.76 (d, *J*=14.7 Hz), 55.26, 51.81, 34.68, 30.65 (d, *J*=3.8 Hz), 28.15, 20.24 (d, *J*=24.2 Hz); EIMS *m*/*z* 310 (M^+), 178, 161; HRMS (EI) *m*/*z* 310.1550 (calcd for $C_{17}H_{23}O_4F$: 310.1579).

*5.9.14. Methyl (2E)-4-formyl-7-(4-methoxyphenyl)-4-methyl-2-heptenoate (**42d**).* Yield 6% (colorless oil); IR (neat) 1725, 1653 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 9.40 (1H, s), 7.06 (2H, d, *J*=8.6 Hz), 6.96 (1H, d, *J*=16.2 Hz), 6.82 (2H, d, *J*=8.6 Hz), 5.84 (1H, d, *J*=16.2 Hz), 3.79 (3H, s), 3.75 (3H, s), 2.55 (2H, t, *J*=7.3 Hz), 1.90–1.46 (4H, m), 1.22 (3H, s); EIMS *m*/*z* 290 (M^+), 278, 258; HRMS (EI) *m*/*z* 290.1503 (calcd for $C_{17}H_{22}O_4$: 290.1517).

*5.9.15. Methyl (3E)-8-(4-methoxyphenyl)-4-methyl-5-oxooct-3-enoate (**43d**).* Yield 73% (colorless oil); IR (neat) 1742, 1671 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.10 (2H, d, *J*=8.6 Hz), 6.82 (2H, d, *J*=8.6 Hz), 6.73 (1H, tq, *J*=6.9, 1.3 Hz), 3.78 (3H, s), 3.73 (3H, s), 3.27 (2H, d, *J*=6.9 Hz), 2.70 (2H, t, *J*=7.5 Hz), 2.58 (2H, t, *J*=7.5 Hz), 1.92 (2H, quintet, *J*=7.5 Hz), 1.78 (3H, d, *J*=1.3 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 201.23, 170.94, 157.78, 139.45, 133.80, 132.44, 129.31 (2C), 113.73 (2C), 55.21, 52.13, 36.45, 34.28, 34.11, 26.31, 11.72; EIMS *m*/*z* 290 (M^+), 177, 134; HRMS (EI) *m*/*z* 290.1524 (calcd for $C_{17}H_{22}O_4$: 290.1517).

*5.9.16. Methyl (2E)-4-fluoro-5-hydroxy-4-methyl-8-(4-methylphenyl)-2-octenoate (**41e**).* Yield 48% (white needles); mp 53–54 °C (hexane). Anal. Calcd for $C_{17}H_{23}O_3F$: C, 69.36; H, 7.88. Found: C, 69.30; H, 7.92. IR ($CHCl_3$) 3618, 1721, 1665 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.09 (2H, d, *J*=8.4 Hz), 7.05 (2H, d, *J*=8.4 Hz), 6.92 (1H, dd, *J*=21.1, 15.8 Hz), 6.10 (1H, d, *J*=15.8 Hz), 3.77 (3H, s), 3.65 (1H, tdd, *J*=10.6, 4.9, 2.3 Hz), 2.64–2.54 (2H, m), 2.31 (3H, s), 1.96–1.80 (1H, m), 1.92 (1H, dt, *J*=4.9, 1.3 Hz), 1.74–1.26 (3H, m), 1.45 (3H, d, *J*=22.3 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 166.40, 146.60 (d, *J*=19.6 Hz), 138.88, 135.21, 129.00 (2C), 128.20 (2C), 120.91 (d, *J*=10.9 Hz), 97.60 (d, *J*=176.0 Hz), 75.71 (d, *J*=24.7 Hz), 51.77, 35.11, 30.67 (d, *J*=3.8 Hz), 27.99, 20.94, 20.24 (d, *J*=24.2 Hz); EIMS *m*/*z* 294 (M^+), 274, 197, 161; HRMS (EI) *m*/*z* 294.1645 (calcd for $C_{17}H_{23}O_3F$: 294.1630).

*5.9.17. Methyl (2E)-4-formyl-4-methyl-7-(4-methylphenyl)-2-heptenoate (**42e**).* Yield 23% (colorless oil); IR (neat) 1727, 1649 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 9.41 (1H, s), 7.09 (2H, d, *J*=7.8 Hz), 7.03 (2H, d, *J*=7.8 Hz), 6.96 (1H, d, *J*=16.4 Hz), 5.84 (1H, d, *J*=16.4 Hz), 3.75 (3H, s), 2.57 (2H, t, *J*=7.8 Hz), 2.31 (3H, s), 1.75–1.48 (4H, m), 1.22 (3H, s); ^{13}C NMR (68 MHz, $CDCl_3$) δ 200.88, 166.34, 148.13, 138.29, 135.50, 129.10 (2C), 128.20 (2C), 122.11, 52.54, 51.74, 35.61, 35.16, 25.85, 20.97, 17.98; EIMS *m*/*z* 274 (M^+), 256, 171; HRMS (EI) *m*/*z* 274.1597 (calcd for $C_{17}H_{22}O_3$: 274.1568).

*5.9.18. Methyl (3E)-4-methyl-8-(4-methylphenyl)-5-oxooct-3-enoate (**43e**).* Yield 9% (colorless oil); IR (neat) 1717, 1653 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.10 (2H, d, *J*=8.8 Hz), 7.06 (2H, d, *J*=8.8 Hz), 6.73 (1H, tq, *J*=6.6, 1.0 Hz), 3.75 (3H, s), 3.27 (2H, d, *J*=6.6 Hz), 2.71 (2H, t, *J*=7.6 Hz), 2.60 (2H, t, *J*=7.6 Hz), 2.32 (3H, s), 1.93 (2H, quintet, *J*=7.6 Hz), 1.78 (3H, d, *J*=1.0 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 201.27, 170.99, 139.53, 138.69, 135.32, 132.44, 129.04 (2C), 128.36 (2C), 52.19, 36.57, 34.80, 34.18, 26.20, 21.00, 11.77; EIMS *m*/*z* 274 (M^+), 248, 201; HRMS (EI) *m*/*z* 274.1576 (calcd for $C_{17}H_{22}O_3$: 274.1568).

*5.9.19. Methyl (2E)-4-fluoro-5-hydroxy-4-methyl-2-decenoate (**41f**).* Yield 54% (colorless oil); IR ($CHCl_3$) 3470, 1729, 1665 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 6.95 (1H, dd, *J*=21.1, 15.7 Hz), 6.11 (1H, d, *J*=15.7 Hz), 3.77 (3H, s), 3.68–3.56 (1H, m), 1.97 (1H, d, *J*=4.6 Hz), 1.65–1.20 (8H, m), 1.46 (3H, d, *J*=22.5 Hz), 0.89 (3H, t, *J*=6.8 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 166.96, 147.31 (d, *J*=19.6 Hz), 121.10 (d, *J*=11.2 Hz), 98.08 (d, *J*=175.8 Hz), 76.34 (d, *J*=25.2 Hz), 52.17, 32.04, 31.52 (d, *J*=3.9 Hz), 26.22, 22.95, 20.85 (d, *J*=24.1 Hz), 14.38; EIMS *m*/*z* 231 (M^+), 201, 149, 133; HRMS (EI) *m*/*z* 231.1414 (calcd for $C_{12}H_{20}FO_3$: 231.1395).

*5.9.20. Methyl (2E)-4-formyl-4-methyl-2-nonenoate (**42f**).* Yield 22% (colorless oil); IR (neat) 1729, 1653 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 9.44 (1H, s), 6.99 (1H, d, *J*=16.2 Hz), 5.87 (1H, d, *J*=16.2 Hz), 3.76 (3H, s), 1.70–1.57 (2H, m), 1.39–1.15 (6H, m), 1.23 (3H, s), 0.88 (3H, t, *J*=6.8 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 201.15, 166.43, 148.42, 121.93, 52.64, 51.73, 35.75, 32.17, 23.63, 22.38, 17.99, 13.94; EIMS *m*/*z* 212 (M^+), 196, 184; HRMS (EI) *m*/*z* 212.1431 (calcd for $C_{12}H_{20}O_3$: 212.1411).

*5.9.21. Methyl (3E)-4-methyl-5-oxodec-3-enoate (**43f**).* Yield 7% (colorless oil); IR (neat) 1744, 1673 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 6.79 (1H, tq, *J*=6.9, 1.3 Hz), 3.74 (3H, s), 3.29 (2H, d, *J*=6.9 Hz), 2.69 (2H, t, *J*=7.5 Hz), 1.79 (3H, d, *J*=1.3 Hz), 1.67–1.54 (2H, m), 1.41–1.18 (4H, m), 0.89 (3H, t, *J*=6.8 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 201.72, 171.04, 139.50, 132.34, 52.16, 37.31, 34.15, 31.51, 24.43, 22.48, 13.93, 11.75; EIMS *m*/*z* 212 (M^+), 196, 184; HRMS (EI) *m*/*z* 212.1441 (calcd for $C_{12}H_{20}O_3$: 212.1411).

5.9.22. (1R,2R*)-1-(Methoxycarbonyl-(E)-ethenyl)-1,2,3,4-tetrahydronaphthalen-2-ol (**44a**).* Yield 65% (colorless oil); IR (neat) 3436, 1725, 1655 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.20–7.10 (3H, m), 7.06–7.00 (1H, m), 6.92 (1H, dd, *J*=15.5, 9.2 Hz), 6.00 (1H, dd, *J*=15.5, 1.0 Hz), 3.94 (1H, ddd, *J*=9.2, 6.3, 3.0 Hz), 3.76 (3H, s), 3.55 (1H, t, *J*=8.1 Hz), 3.03–2.82 (2H, m), 2.20–2.09 (1H, m), 1.94–1.79 (2H, m); ^{13}C NMR (68 MHz, $CDCl_3$) δ 166.59, 149.35, 135.50, 134.02, 129.56, 128.86, 126.82, 126.12, 124.29, 69.97, 51.56, 51.38, 29.04, 26.84; EIMS *m*/*z* 232 (M^+), 214, 200, 181, 156, 128, 115; HRMS (EI) *m*/*z* 232.1107 (calcd for $C_{14}H_{16}O_3$ 232.1099).

5.9.23. (1R,2R*)-6-Methoxy-1-(methoxycarbonyl-(E)-ethenyl)-1,2,3,4-tetrahydronaphthalen-2-ol (**44b**).* Yield 65% (white needles); mp 88 °C (hexane/toluene=2/1). Anal. Calcd for $C_{15}H_{18}O_4$: C, 68.69; H, 6.92. Found: C, 68.55; H, 6.98. IR ($CHCl_3$) 3442, 1719, 1655 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 6.94 (1H, d, *J*=8.5 Hz), 6.90 (1H, dd, *J*=15.5, 9.2 Hz), 6.72 (1H, dd, *J*=8.5, 2.7 Hz), 6.66 (1H, d, *J*=2.7 Hz), 5.97 (1H, d, *J*=15.5 Hz), 3.94–3.83 (1H, m), 3.78 (3H, s), 3.75 (3H, s), 3.49 (1H, t, *J*=8.2 Hz), 3.00–2.78 (2H, m), 2.18–2.06 (1H, m), 1.99–1.78 (2H, m); ^{13}C NMR (68 MHz, $CDCl_3$) δ 166.58, 158.47, 149.56, 136.81, 130.67, 126.09, 124.23, 113.51, 112.55, 70.25, 55.24, 51.59, 50.93, 29.02, 27.15; EIMS *m*/*z* 262 (M^+), 244, 230, 159; HRMS (EI) *m*/*z* 262.1224 (calcd for $C_{15}H_{18}O_4$: 262.1204).

5.9.24. (1R,2R*)-8-Methoxy-1-(methoxycarbonyl-(E)-ethenyl)-1,2,3,4-tetrahydronaphthalen-2-ol (**45b**).* Yield 35% (white needles); mp 117 °C (hexane/toluene=1:1). Anal. Calcd for $C_{15}H_{18}O_4$: C, 68.69; H, 6.92. Found: C, 68.74; H, 6.99. IR ($CHCl_3$) 3442, 1719, 1655 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.16 (1H, t, *J*=7.9 Hz), 6.98 (1H, dd, *J*=15.7, 6.6 Hz), 6.76 (1H, d, *J*=7.9 Hz), 6.69 (1H, d, *J*=7.9 Hz), 5.58 (1H, dd, *J*=15.7, 1.6 Hz), 4.25–4.18 (1H, m), 3.95–3.88 (1H, m), 3.75 (3H, s), 3.70 (3H, s), 2.98 (1H, ddd, *J*=17.6, 10.0, 7.6 Hz), 2.76 (1H, ddd, *J*=17.6, 5.9, 3.9 Hz), 2.05–1.88 (2H, m), 1.65 (1H, d, *J*=5.4 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 167.23, 158.17, 149.55, 137.03, 127.57, 121.98, 121.63, 121.28, 107.80, 68.51, 55.25, 51.42, 43.87, 25.17, 23.62; EIMS *m*/*z* 262 (M^+), 244, 230, 159; HRMS (EI) *m*/*z* 262.1183 (calcd for $C_{15}H_{18}O_4$: 262.1204).

5.9.25. (1R,2R*)-6,7-Dimethoxy-1-(methoxycarbonyl-(E)-ethenyl)-1,2,3,4-tetrahydronaphthalen-2-ol (**44c**).* Yield 84% (colorless oil); IR (neat) 3496, 1723, 1653 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 6.92 (1H, dd, *J*=15.6, 9.0 Hz), 6.61 (1H, s), 6.48 (1H, s), 5.97 (1H, dd, *J*=15.6,

0.9 Hz), 3.96–3.88 (1H, m), 3.85 (3H, s), 3.81 (3H, s), 3.76 (3H, s), 3.55–3.45 (1H, m), 2.95–2.73 (2H, m), 2.16–2.04 (1H, m), 1.93–1.77 (2H, m); ^{13}C NMR (68 MHz, $CDCl_3$) δ 166.55, 149.59, 148.11, 147.59, 127.66, 125.57, 124.18, 112.30, 111.51, 70.09, 56.02, 55.86, 51.62, 51.05, 28.85, 26.28; EIMS *m*/*z* 292 (M^+), 274, 189; HRMS (EI) *m*/*z* 292.1290 (calcd for $C_{16}H_{20}O_5$: 292.1310).

5.9.26. (1R,2R*)-7,8-Dimethoxy-1-(methoxycarbonyl-(E)-ethenyl)-1,2,3,4-tetrahydronaphthalen-2-ol (**45c**).* Yield 16% (colorless oil); IR (neat) 3448, 1723, 1653 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.01 (1H, dd, *J*=15.6, 7.1 Hz), 6.86 (1H, d, *J*=8.4 Hz), 6.81 (1H, d, *J*=8.4 Hz), 5.64 (1H, dd, *J*=15.6, 1.5 Hz), 4.21–4.12 (1H, m), 3.95–3.88 (1H, m), 3.83 (3H, s), 3.76 (3H, s), 3.69 (3H, s), 2.91 (1H, ddd, *J*=17.0, 10.0, 6.8 Hz), 2.72 (1H, ddd, *J*=17.0, 6.1, 4.3 Hz), 2.01–1.79 (2H, m), 1.74 (1H, br); ^{13}C NMR (68 MHz, $CDCl_3$) δ 167.04, 150.68, 149.77, 147.84, 128.57, 127.62, 124.10, 122.06, 111.98, 68.69, 60.42, 55.87, 51.47, 44.79, 25.65, 23.23; EIMS *m*/*z* 292 (M^+), 274, 189; HRMS (EI) *m*/*z* 292.1287 (calcd for $C_{16}H_{20}O_5$: 292.1310).

5.9.27. (1R,2R*)-7-Methoxy-1-(methoxycarbonyl-(E)-ethenyl)-1,2,3,4-tetrahydronaphthalen-2-ol (**44d**).* Yield 98% (colorless oil); IR (neat) 3440, 1723, 1649 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (1H, d, *J*=8.4 Hz), 6.91 (1H, dd, *J*=15.5, 8.6 Hz), 6.74 (1H, dd, *J*=8.4, 2.5 Hz), 6.55 (1H, d, *J*=2.5 Hz), 5.99 (1H, d, *J*=15.5 Hz), 3.96–3.88 (1H, m), 3.75 (6H, s), 3.52 (1H, t, *J*=8.6 Hz), 2.95–2.77 (2H, m), 2.18–2.08 (1H, m), 1.91–1.79 (2H, m); ^{13}C NMR (68 MHz, $CDCl_3$) δ 166.53, 157.86, 149.15, 135.17, 129.81, 127.54, 124.38, 114.51, 112.91, 70.05, 55.25 (2C), 51.57, 29.24, 25.98; EIMS *m*/*z* 262 (M^+), 244, 159; HRMS (EI) *m*/*z* 262.1224 (calcd for $C_{15}H_{18}O_4$: 262.1204).

5.9.28. (1R,2R*)-6-Methoxy-1-(methoxycarbonyl-(E)-ethenyl)-1-methyl-1,2,3,4-tetrahydronaphthalen-2-ol (**46b**).* Yield 34% (colorless oil); IR (neat) 3484, 1723 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.01 (1H, d, *J*=15.8 Hz), 6.96 (1H, d, *J*=8.5 Hz), 6.72 (1H, dd, *J*=8.5, 2.9 Hz), 6.63 (1H, d, *J*=2.9 Hz), 5.84 (1H, d, *J*=15.8 Hz), 3.92 (1H, dd, *J*=8.9, 4.0 Hz), 3.77 (3H, s), 3.74 (3H, s), 3.02–2.80 (2H, m), 2.05–1.88 (2H, m), 1.57 (1H, br), 1.39 (3H, s); ^{13}C NMR (68 MHz, $CDCl_3$) δ 167.06, 158.13, 156.06, 136.05, 131.76, 129.77, 121.23, 113.29, 112.71, 72.86, 55.15, 51.55, 46.40, 27.32, 26.09, 20.99; EIMS *m*/*z* 276 (M^+), 244, 187, 173; HRMS (EI) *m*/*z* 276.1336 (calcd for $C_{16}H_{20}O_4$: 276.1360).

5.9.29. (1R,2R*)-8-Methoxy-1-(methoxycarbonyl-(E)-ethenyl)-1-methyl-1,2,3,4-tetrahydronaphthalen-2-ol (**47b**).* Yield 56% (colorless oil); IR (neat) 3472, 1717, 1647 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.14 (1H, d, *J*=16.0 Hz), 7.13 (1H, t, *J*=7.9 Hz), 6.72 (1H, dd, *J*=7.9, 0.8 Hz), 6.68 (1H, d, *J*=7.9 Hz), 5.85 (1H, d, *J*=16.0 Hz), 3.86–3.71 (1H, m), 3.74 (3H, s), 3.69 (3H, s), 2.91 (2H, dd, *J*=8.4, 4.8 Hz), 2.09–1.82 (3H, m), 1.44 (3H, s); ^{13}C NMR (68 MHz, $CDCl_3$) δ 167.57, 158.23, 158.13, 136.51, 129.81, 127.53, 121.59, 117.93, 109.18, 72.65, 55.08, 51.35, 45.13, 28.66, 25.63, 16.58; EIMS *m*/*z* 276 (M^+), 244, 187, 173; HRMS (EI) *m*/*z* 276.1354 (calcd for $C_{16}H_{20}O_4$: 276.1360).

Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research (C) (15590017 to S.N.).

References and notes

1. Taylor, S. K.; Hockerman, G. H.; Karrick, G. L.; Lyle, S. B.; Schramm, S. B. *J. Org. Chem.* **1983**, *48*, 2449.
2. Taylor, S. K.; Davisson, M. E.; Hissom, B. R., Jr.; Brown, S. L.; Pristach, H. A.; Schramm, S. B.; Harvey, S. M. *J. Org. Chem.* **1987**, *52*, 425.
3. Taylor, S. K.; Blankespoor, C. L.; Harvey, S. M.; Richardson, L. J. *J. Org. Chem.* **1988**, *53*, 3309.
4. Nicolaou, K. C.; Prasad, C. V. C.; Somers, P. K.; Hwang, C.-K. *J. Am. Chem. Soc.* **1989**, *111*, 5330 5335.
5. Stork, G.; Kobayashi, Y.; Suzuki, T.; Zhao, K. *J. Am. Chem. Soc.* **1990**, *112*, 1661.
6. (a) Akita, H.; Umezawa, I.; Takano, M.; Matsukura, H.; Oishi, T. *Chem. Pharm. Bull.* **1991**, *39*, 3094; (b) Ono, M.; Todoriki, R.; Yamamoto, Y.; Akita, H. *Chem. Pharm. Bull.* **1994**, *42*, 1590; (c) Ono, M.; Yamamoto, Y.; Todoriki, R.; Akita, H. *Heterocycles* **1994**, *37*, 181; (d) Ono, M.; Yamamoto, Y.; Akita, H. *Chem. Pharm. Bull.* **1995**, *43*, 553.
7. For preliminary report from our lab, see: Nagumo, S.; Miyoshi, I.; Akita, H.; Kawahara, N. *Tetrahedron Lett.* **2002**, *43*, 2223.
8. House, H. O. *J. Am. Chem. Soc.* **1956**, *78*, 2298; (b) House, H. O.; Wasson, R. L. *J. Am. Chem. Soc.* **1956**, *78*, 4394; (c) House, H. O.; Ryerson, G. D. *J. Am. Chem. Soc.* **1961**, *83*, 979; (d) Maruoka, K.; Hasegawa, M.; Yamamoto, H.; Suzuki, K.; Shimazaki, M.; Tsuchihashi, G. *J. Am. Chem. Soc.* **1986**, *108*, 3827; (e) Suzuki, K.; Miyazawa, M.; Tsuchihashi, G. *Tetrahedron Lett.* **1987**, *28*, 3515; (f) Maruoka, K.; Ooi, T.; Yamamoto, H. *J. Am. Chem. Soc.* **1989**, *111*, 6431; (g) Maruoka, K.; Nagahara, S.; Ooi, T.; Yamamoto, H. *Tetrahedron Lett.* **1989**, *30*, 5607; (h) Enev, V. S.; Tsankova, E. T. *Tetrahedron* **1991**, *47*, 6399; (i) Maruoka, K.; Ooi, T.; Nagahara, S.; Yamamoto, H. *Tetrahedron* **1991**, *47*, 6983; (j) Maruoka, K.; Ooi, T.; Yamamoto, H. *Tetrahedron* **1992**, *48*, 3303; (k) Jung, M. E.; Dámico, D. C. *J. Am. Chem. Soc.* **1995**, *117*, 7379; (l) Takanami, T.; Hirabe, R.; Ueno, M.; Hino, F.; Suda, K. *Chem. Lett.* **1996**, 1031; (m) Suda, K.; Baba, K.; Nakajima, S.; Takanami, T. *Tetrahedron Lett.* **1999**, *40*, 7243; (n) Hara, N.; Mochizuki, A.; Tatara, A.; Fujimoto, Y. *Tetrahedron: Asymmetry* **2000**, *11*, 1859; (o) Kita, Y.; Furukawa, A.; Futamura, J.; Higuchi, K.; Ueda, K.; Fujioka, H. *Tetrahedron* **2001**, *57*, 815; (p) Suda, K.; Baba, K.; Nakajima, S.; Takanami, T. *Chem. Commun.* **2002**, 2570; (q) Suda, K.; Kikkawa, T.; Nakajima, S.; Takanami, T. *J. Am. Chem. Soc.* **2004**, *126*, 9554.
9. For the formation of fluorohydrin from epoxide with $BF_3\cdot Et_2O$, see: (a) Goldsmith, D. J. *J. Am. Chem. Soc.* **1962**, *84*, 3913; (b) Berti, G.; Macchia, B.; Macchia, F.; Monti, L. *J. Chem. Soc. C* **1971**, 3371; (c) Barili, P. L.; Belluci, G.; Berti, G.; Macchia, B.; Macchia, F. *J. Chem. Soc., Perkin Trans. 1* **1974**, 477; (d) Takaishi, N.; Takahashi, H.; Inamoto, Y. *Tetrahedron Lett.* **1985**, *26*, 2361; (e) Duhamel, P.; Leblond, B.; Poirier, J.-M. *J. Chem. Soc., Chem. Commun.* **1993**, 476.
10. Formation of conjugated ketones **43b**, **43d**, **43e**, and **43f** includes migration of double bond. The rearrangement occurs when the corresponding reaction mixture is purified by column chromatography with silica gel.
11. (a) Pigge, F. C.; Coniglio, J. J.; Rath, N. P. *Org. Lett.* **2003**, *5*, 2011; (b) Pegge, F. C.; Coniglio, J. J.; Rath, N. P. *J. Org. Chem.* **2004**, *69*, 1161.