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Nucleophilic addition reaction of aromatic compounds with α-chloroglycidates in the presence of Lewis acid

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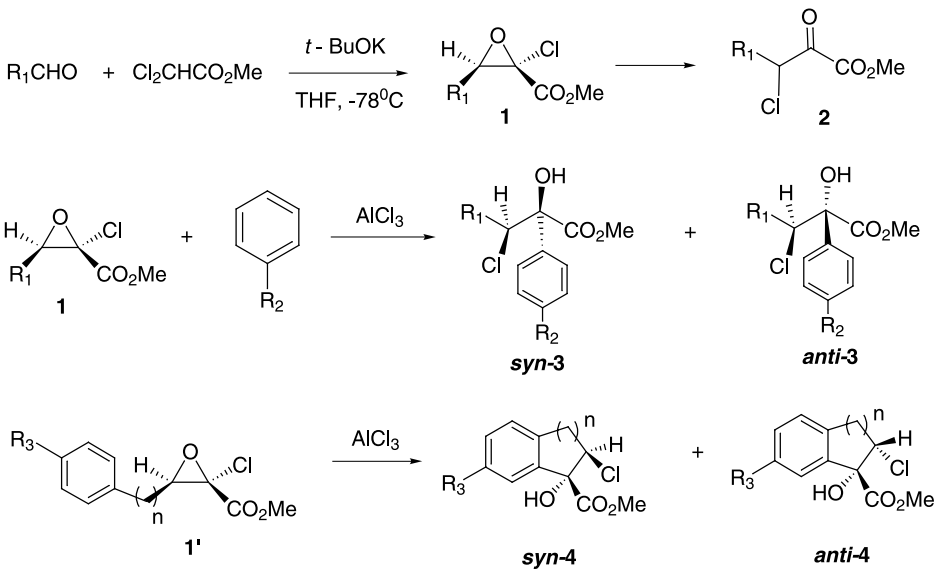
Abstract—The epoxide **1** obtained by the Darzens condensation reaction of aldehydes with methyl dichloroacetate, reacted with aromatic compounds in the presence of aluminium chloride to afford α-aryl-β-chloro-α-hydroxyalkanoate **3**. The intra-molecular nucleophilic addition of epoxide **1′** gave cyclisation compound **4**. The scope and limitation of these reaction were studied for various aldehydes and aromatic compounds. The reaction was also studied in the presence of aluminium chloride supported on alumina or silica gel, which is thought to be a mild Lewis acid and harmless for environment.

1. Introduction

Friedel–Crafts reaction is one of the most typical chemical reaction.[1] However, concerning the reaction of epoxides with aromatic compounds in the presence of Lewis acid, some reactions using only simple epoxides are reported. In 1960s, Hata et al. reported the reaction of epoxides with benzene or alkylbenzene in the presence of some Lewis acids.[2] Nakamoto et al. studied Friedel–Crafts alkylation of benzene with some oxiranes and oxetanes.[3] In 1970s, Nakajima et al. reported asymmetric induction in the Friedel–Crafts reaction of benzene with (+)-1,2-epoxybutane.[4] Inoue et al. examined the reaction of toluene and anisole with 2-methyloxirane and 2,3-dimethyloxirane.[5]



Scheme 1.

Keywords: Darzens reactions; addition reactions; epoxides; cyclisation.

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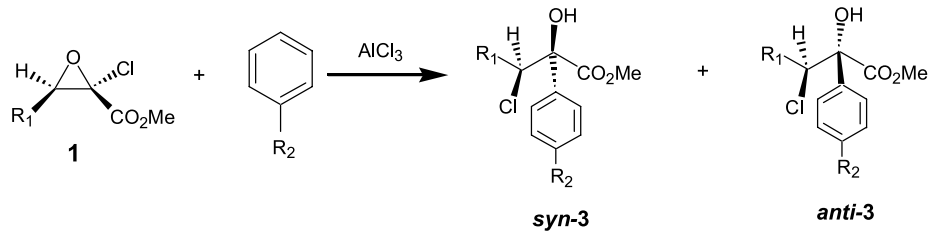
Table 1. Reaction of 2-chloro-2,3-epoxyalkanoates with aromatic compounds in the presence of Lewis acid



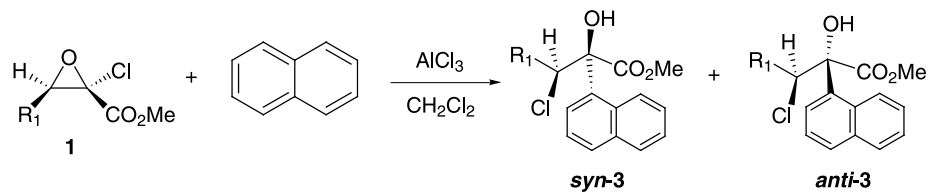
Entry	R_1	R_2	Lewis acid	Conditions	Yield	*syn/anti*
1	$CH_3(CH_2)_4-$	H	$AlCl_3$	rt, 1 h	**3a**, 58.8%	82/18
2	$CH_3(CH_2)_8-$	H	$AlCl_3$	rt, 1 h	**3b**, 76.8%	81/19
3	$(CH_3)_2CH-$	CH_3-	$AlCl_3$	rt, 50 min	**3c**, 55.9%	79/21
4	$CH_3(CH_2)_4-$	CH_3-	$AlCl_3$	rt, 40 min	**3d**, 65.4%	77/23
5	$CH_3(CH_2)_6-$	CH_3-	$AlCl_3$	rt, 40 min	**3e**, 71.4%	78/22
6	$CH_3(CH_2)_8-$	CH_3-	$AlCl_3$	rt, 40 min	**3f**, 80.7%	79/21
7	$CH_3(CH_2)_2-$	CH_3CH_2-	$AlCl_3$	rt, 1 h	**3g**, 60.1%	77/23
8	$CH_3(CH_2)_4-$	CH_3CH_2-	$AlCl_3$	rt, 50 min	**3h**, 63.6%	81/19
9	$CH_3(CH_2)_6-$	CH_3CH_2-	$AlCl_3$	rt, 50 min	**3i**, 74.2%	77/23
10	$CH_3(CH_2)_8-$	CH_3CH_2-	$AlCl_3$	rt, 50 min	**3j**, 81.3%	79/21
11	$CH_3(CH_2)_2-$	$CH_3(CH_2)_3-$	$AlCl_3$	rt, 50 min	**3k**, 62.3%	81/19
12	$CH_3(CH_2)_4-$	$CH_3(CH_2)_3-$	$AlCl_3$	rt, 50 min	**3l**, 68.0%	79/21
13	$CH_3(CH_2)_6-$	$CH_3(CH_2)_3-$	$AlCl_3$	rt, 50 min	**3m**, 76.3%	78/22
14	$CH_3(CH_2)_8-$	$CH_3(CH_2)_3-$	$AlCl_3$	rt, 50 min	**3n**, 87.4%	77/23
15	$(CH_3)_2CH-$	CH_3-	$TiCl_4$	50°C, 2 h	**3c**, 13.8%;**2c**, 56.5%	79/21
16	$(CH_3)_2CH-$	CH_3-	$FeCl_3$	rt, 2 h	**3c**, 14.4%;**2c**, 52.3%	79/21

In 1980s, Taylor et al. studied highly stereoselective Friedel–Crafts alkylations via epoxide transannular reactions, and Friedel–Crafts cycloalkylations of some epoxides.[6] In our laboratory, we have been studied Darzens condensation for more than 20 years.[7]

Using the product obtained by Darzens condensation, we have carried out various reactions. As a link of this study, we examined the reaction of α-chloro-α,β-epoxyalkanoates (**1**) with aromatic compounds in the presence of Lewis acid (Scheme 1). Interestingly, this reaction did not give Friedel–Crafts reaction product, but a nucleophilic addition product of aromatic compounds to **1**, α-aryl-β-chloro-α-hydroxyalkanoate (**3**). Lewis acid-promoted addition reaction of aromatic compounds to α-chloroglycidates **1** to give alcohol **3** has never been reported, and we reported it as a communication previously.[8] On the other hand, the intramolecular nucleohpilic addition of the epoxide **1′** in the presence of aluminium chloride furnished a cyclisation product **4** as our expectations (Scheme 1). Here, we report the results about this intra-molecular cycloaddition reaction and the detail experimental data of alcohol **3**. In 1974, Coutrot et al. has obtained compound **3** by the addition of organomagnesium compounds to β-chloro-α-ketoesters.[9]

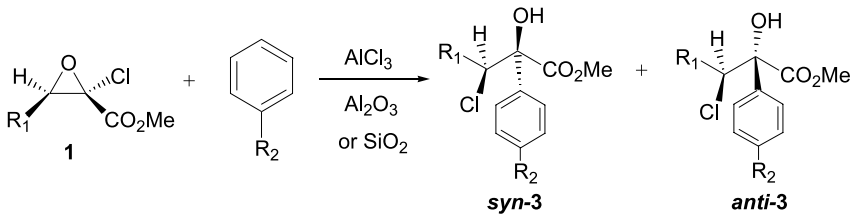
2. Results and discussion

By Darzens condensation, aldehydes react with methyl dichloroacetate in the presence of potassium *tert*-butoxide at −78°C to give α-chloro-α,β-epoxyalkanoates (**1** or **1′**) in good yields, which can be rearranged to afford isomerization products (**2**). Then, the reaction of α-chloro-α,β-epoxyalkanoates (**1**) with aromatic compounds was carried out in the presence of $AlCl_3$. The results are shown in Table 1. α-Aryl-β-chloro-α-hydroxyalkanoates (**3**) were obtained in 55.9–87.4% yield and major product was *syn* isomer. The structure of *syn*-**3** was confirmed by single-crystal X-ray analysis of *syn*-**3c** (R_1=*i*-Pr, R_2=CH_3).[8] When the substrate R_1 became long, the reaction was more active, and the yield became high (entries 3–6, 7–10, 11–14). The reactivity of aromatic compounds was found as the following order; benzene<toluene<ethylbenzene<*n*-butylbenzene (entries 1, 4, 8 and 12 for R_1=$CH_3(CH_2)_4-$; entries 2, 6, 10 and 14 for R_1=$CH_3(CH_2)_8-$). Moreover, we tried with other aromatic compounds, and in the case of naphthalene, the addition products were obtained in good yields of (47–84%) (Scheme 2). But, in the case of anthracene or *N*,*N*-dimethylaniline, the addition product was obtained in low yields (31–35%). On the other hand, the reaction of aniline



Scheme 2. Reaction of 2-chloro-2,3-epoxyalkanoates with naphthalene in the presence of $AlCl_3$.

Table 2. Reaction of 2-chloro-2,3-epoxyalkanoates with aromatic compounds in the presence of $AlCl_3$ supported on Al_2O_3 or SiO_2



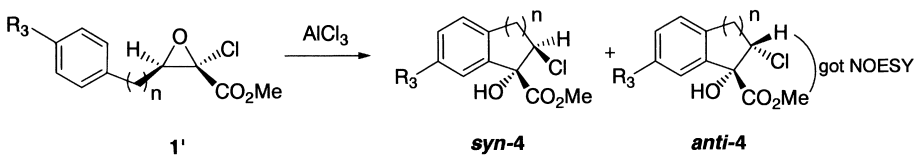
Entry	R_1	R_2	Conditions	Yield	*syn/anti*
1	$(CH_3)_2CH-$	CH_3-	$AlCl_3/Al_2O_3$=1:2; rt, 40 min	**3c**, 66.5%	82/18
2	$(CH_3)_2CH-$	CH_3-	$AlCl_3/Al_2O_3$=1:5; rt, 40 min	**3c**, 56.7%	80/20
3	$(CH_3)_2CH-$	CH_3-	$AlCl_3/Al_2O_3$=1:10; rt, 40 min	**3c**, 49.5%	76/24
4	$CH_3(CH_2)_4-$	H	$AlCl_3/Al_2O_3$=1:2; rt, 1 h	**3a**, 64.8%	83/17
5	$CH_3(CH_2)_8-$	H	$AlCl_3/Al_2O_3$=1:2; rt, 50 min	**3b**, 92.2%	84/16
6	$(CH_3)_2CH-$	CH_3-	$AlCl_3/SiO_2$=1:2; rt, 1 h	**3c**, 61.1%	81/21
7	$(CH_3)_2CH-$	CH_3-z	$AlCl_3/SiO_2$=1:5; rt, 1 h	**3c**, 53.7%	78/22
8	$(CH_3)_2CH-$	CH_3-	$AlCl_3/SiO_2$=1:10; rt, 1 h	**3c**, 47.3%	78/22
9	$CH_3(CH_2)_4-$	H	$AlCl_3/SiO_2$=1:2; rt, 1 h	**3a**, 55.1%	81/19
10	$CH_3(CH_2)_8-$	H	$AlCl_3/SiO_2$=1:2; rt, 1 h	**3b**, 67.1%	75/25

or phenol gave the addition product only in poor yields (15–18%). In the case of bromobenzene or nitrobenzene, the reaction gave no product. The influence of the quantity of $AlCl_3$ added was also studied, and it was found that its 3 equiv. was the optimum quantity. With increasing the quantities (5, 10 equiv.), the yield became lower and there was no influence on the stereochemistry.[8]

To search the better Lewis acid, the reaction was studied in the presence of $TiCl_4$ or $FeCl_3$ besides $AlCl_3$. But unsatisfied results were obtained, and the addition product was obtained in very poor yield. The isomerization prevailed in such case to give β-chloro-α-oxoalkanoates (**2**) in good yields (entries 15, 16). Furthermore, we also investigated this reaction in the presence of aluminium chloride supported on alumina or silica gel, which is thought to be a mild Lewis acid and harmless for environment (Table 2). In the case of reactions in the presence of $AlCl_3$ supported on Al_2O_3, the stereoselectivities changed well somewhat, although the yield of addition products **3** became higher than that of only in the presence of $AlCl_3$ (entries 4 and 5). In the case of reactions in the presence of $AlCl_3$ supported on SiO_2, the yield of addition products **3** depends on the nature of substrate (entries 6, 9 and 10). In all cases the stereoselectivities were not changed so much. Then, we examined the effects of the ratio of $AlCl_3/Al_2O_3$ or SiO_2, and among the ratio of 1:2, 1:5 and 1:10, 1:2 ratio of $AlCl_3$ supported on Al_2O_3 or SiO_2 afforded the highest yield (entries 1, 6).

Considering the generality of this reaction, we carried out the reaction of epoxide **1′** in the presence of $AlCl_3$. As we expected, cyclisation products **4** were furnished in good yields of 63.5–93.2% (Table 3). In the case of 5-membered ring, the solvent CH_2Cl_2 was better than $(CH_2Cl)_2$ (entries 1, 3). The stereoselectivity depends on the reaction temperature (entries 2, 3). In the case of 6-membered ring, the solvent $(CH_2Cl)_2$ was found better (entries 4, 5). In the case

Table 3. The intra-molecular cycloaddition reaction of 2-chloro-2,3-epoxyalkanoates 1′ in the presence of $AlCl_3$



Entry	R_3	*n*	$AlCl_3$ (equiv.)	Solvent	Conditions	Yield	*anti/syn*
1	H	1	1	$(CH_2Cl)_2$	0°C, 40 min	**4a**, 59.7%	79/21[a]
2	H	1	1	CH_2Cl_2	rt, 35 min	**4a**, 38.5%[b]	100/0
3	H	1	2	CH_2Cl_2	0°C., 1 h	**4a**, 63.5%	0/100
4	H	2	1	$(CH_2Cl)_2$	0°C, 2 h	**4b**, 80.9%	40/60
5	H	2	1	CH_2Cl_2	0°C, 2 h	**4b**, 62.7%	35/65
6	H	3	3	$(CH_2Cl)_2$	0°C, 2 h	**4c**, 64.1%	100/0
7	H	3	3	CH_2Cl_2	0°C, 2 h	**4c**, 63.0%	100/0
8	CH_3O-	1	1	$(CH_2Cl)_2$	0°C, 3 h; rt, 3 h	**4d**, 63.1%[c]	43/57[a]
9	CH_3O-	1	3	CH_2Cl_2	0°C, 3 h	**4d**, 85.4%	60/40
10	CH_3O-	1	3	CH_2Cl_2	rt, 2 h	**4d**, 86.7%	75/25
11	CH_3O-	2	3	$(CH_2Cl)_2$	r.t, 1 h	**4e**, 93.2%	39/61

[a] Stereoslectivity was determined by GC-Mass.
[b] Yield of isomerized product was 28.6%.
[c] Recovery was 20.6%.

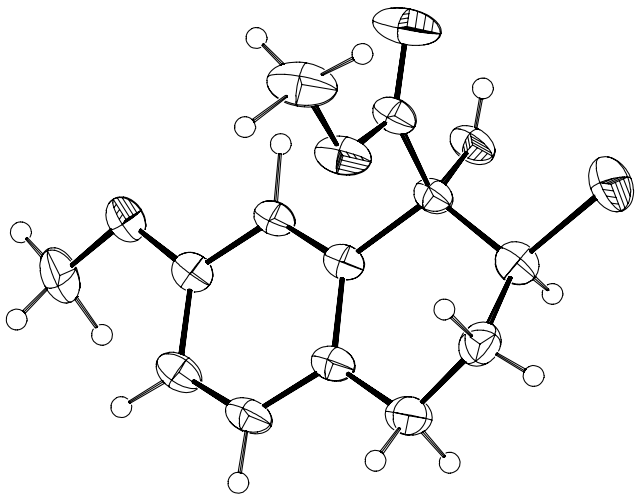


Figure 1. Geometry of molecule *syn*-**4e** in crystal.

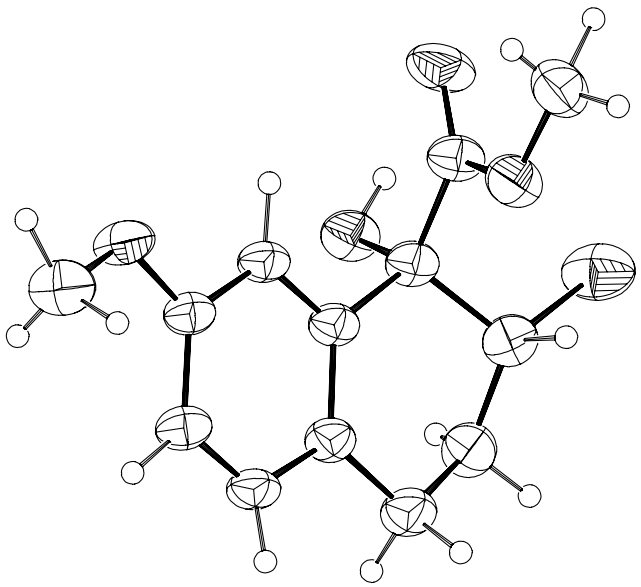


Figure 2. Geometry of molecule *anti*-**4e** in crystal.

of 7-membered ring, only *anti* product was obtained (entries 6, 7). When phenyl ring is substituted with electron donating group like OMe, the cycloaddition reaction became predominant, and the yield of product **4** became higher (entries 8–11). The structure of *syn*-**4** was confirmed by single-crystal X-ray analysis of *syn*-**4e** and *anti*-**4e** (R_3=OMe, n=2). Figures 1 and 2 illustrate the geometrical aspect of the molecule and explain the chemical structure reasonably. Configuration of *anti*-**4** was also confirmed by NOESY.

We think that the chlorine in epoxide **1** or **1′** plays an important role in these nucleophilic reactions. So, the reaction of epoxide **5** in the presence of $AlCl_3$ was carried out, which epoxide **5** was obtained by Darzens reaction of 3-phenylpropionaldehyde with methyl chloroacetate. This reaction did not give cycloaddition product **4**, but a ring-opened product of diol **6** in good yield (98%) as anticipated (Scheme 3). To study the mechanism of this intra-molecular cycloaddition reaction, the reaction of α-chloro-β-oxo-alkanoate **2** obtained by the isomerization of epoxide **1′** in the presence of $AlCl_3$ was carried out. This reaction gave cycloaddition product **4d** in 84% yield (Scheme 4).

Thus, a cnsiderable mechanism of the cycloaddition reaction is shown in Scheme 4.

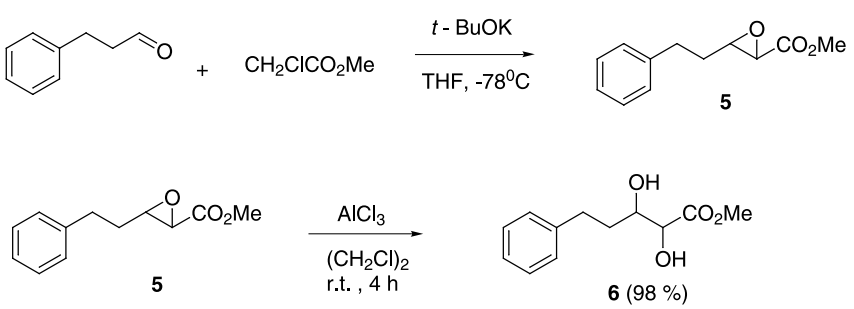
In summary, it is found that the reaction of α-chloro-α,β-epoxyalkanoates with aromatic compounds in the presence of Lewis acid gives α-aryl-β-chloro-α-hydroxyalkanoates in stead of Friedel–Crafts reaction products, and the major product is *syn* isomer. The intra-molecular cycloaddition reaction gives cyclisation product in good yield. This nucleophilic addition reaction can be utilized in the synthesis of donaxaridine.[10] Utilizing of this cycloaddition reaction, the total synthesis of a natural product, (−)-Galanthamine[11] is currently under investigation.

3. Experimental

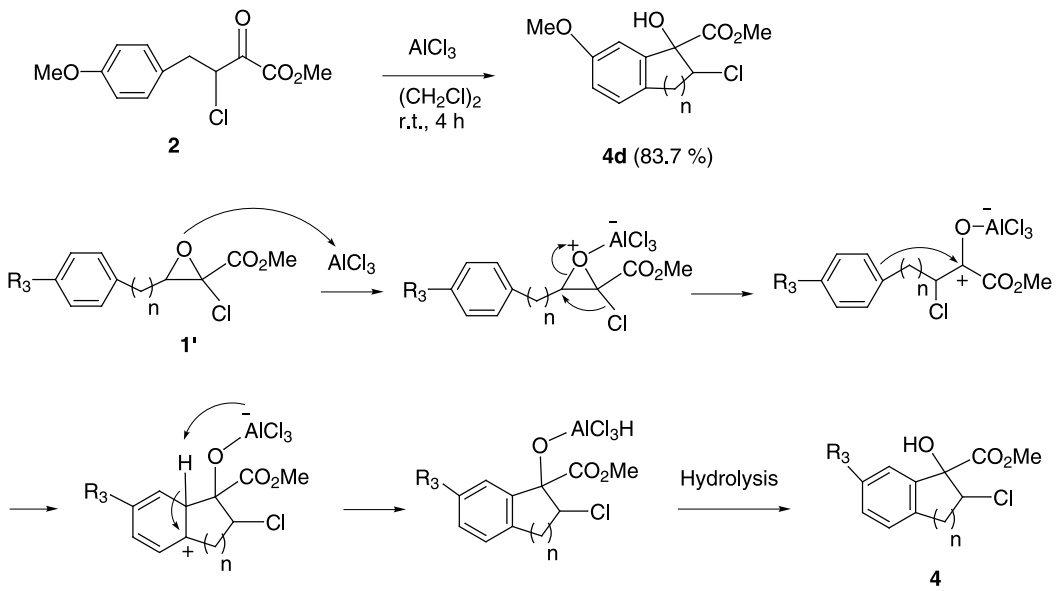
3.1. General procedure

All reactions were carried out under nitrogen atmosphere with dry, freshly distilled solvents and under anhydrous condition. Tetrahydrofuran (THF) was distilled from sodium benzophenone before use. Methylene chloride (CH_2Cl_2), benzene, and toluene were distilled from calcium hydride.

Reagents of the highest commercial quality were purchased and used without further purification. Reactions were monitored by thin-layer chromatography (TLC) on 0.25 mm E. Merck silica gel plates (60F-254) using UV light and/or 5% ethanonic phosphomolybdic acid. E. Merck silic gel (60, particle size 0.040–0.050 mm) was used for flash column chromatography.



Scheme 3. Study of the role of chlorine in epoxide **1**.



Scheme 4. Proposed mechanism of the intra-molecular cycloaddtion reaction.

NMR spectra were recorded on Varian Gemini 200 or JEOL 300 MHz instruments and calibrated using residual undeuterated solvent as an internal reference. IR spectra were recorded on a JASCO FT-IR 5000 spectrometer or Avatar 360T2 FT-IR spectrometer (Thermo Nicolet model). Elementary analysis was carried out on a Perkin–Elmer 2400 Series II CHNS/O Analyzer.

3.2. Preparation of starting materials

All 2-chloro-2,3-epoxyalkanoates were prepared by Darzen condensation of aldehydes and methyl dichloroacetate.[7]

3.3. General procedure for the preparation of compounds 3

To a stirring solution of aluminium chloride (400 mg, 3 mmol) in CH_2Cl_2 (4 mL) was added the solution of methyl 2-chloro-2,3-epoxyalkanoate **1**(1 mmol) and aromatic compound (1 mmol) in CH_2Cl_2 (2 mL) at room temperature. The mixture was stirred for 1 h, then stopped by pouring the ice (10 mL), the aqueous layer was extracted with EtOAc, and the combined extracts were washed with saturated $NaHCO_3$ solution and brine, then dried over $MgSO_4$. Evaporation of the solvent gave a clean oil, which was further purified by column chromatography as indicated below.

3.3.1. Methyl (±)-2-hydroxy-2-phenyl-3-chlorooctanoate (3a). The crude product was purified by column chromatography (hexane/ether=160/1) to give 137 mg (48.2%) of (*S*,*S*)-(±)-**3a** and 30 mg (10.6%) of (*S*,*R*)-(±)-**3a**. (*S*,*S*)-(±)-**3a**; colorless liquid, R_f=0.40 (hexane/ether=2/1); ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.82 (t, *J*=6.8 Hz, 3H), 1.16–1.75 (m, 8H), 3.83 (s, 3H), 3.93 (s, 1H), 4.68 (dd, *J*=2.2, 11.0 Hz, 1H), 7.32–7.69 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.89, 22.36, 26.22, 30.53, 30.85, 53.63, 68.26, 81.28, 125.91, 128.38, 128.51, 137.73, 173.44; IR (neat): 3514, 2958, 2932, 2864, 1742, 1450, 1257, 1075, 731 cm^{-1}. Anal. calcd for $C_{15}H_{21}ClO_3$: C, 63.26; H, 7.43. Found: C, 63.31; H, 7.78. (*S*,*R*)-(±)-**3a**; colorless liquid, R_f=0.25 (hexane/ether=2/1); ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.91 (t, *J*=6.4 Hz, 3H), 1.29–2.10 (m, 8H), 3.76 (s, 1H),3.82 (s, 3H), 4.61 (dd, *J*=1.6, 10.8 Hz, 1H), 7.36–7.66 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.97, 22.43, 26.57, 31.06, 33.14, 53.66, 67.57, 81.34, 125.79, 128.33, 133.35, 139.39, 172.99; IR (neat): 3512, 2959, 2928, 2854, 1737, 1458, 1247, 1135, 757 cm^{-1}. Anal. calcd for $C_{15}H_{21}ClO_3$: C, 63.26; H, 7.43. Found: C, 63.31; H, 7.78.

3.3.2. Methyl (±)-2-hydroxy-2-phenyl-3-chlorododecanoate (3b). The crude product was purified by column chromatography (hexane/ether=160/1) to give 212 mg (62.2%) of (*S*,*S*)-(±)-**3b** and 50 mg (14.6%) of (*S*,*R*)-(±)-**3b**. (*S*,*S*)-(±)-**3b**; colorless liquid, R_f=0.40 (hexane/EtOAc=2/1); ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.88 (t, *J*=6.4 Hz, 3H), 1.23–1.75 (m, 16H), 3.83 (s, 3H), 4.00 (s, 1H), 4.71 (dd, *J*=1.6, 11.2 Hz, 1H), 7.33–7.73 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.00, 22.56, 26.43, 28.56, 29.16, 29.22, 29.34, 30.46, 31.75, 53.49, 68.17, 81.23, 125.86, 128.29, 128.42, 137.72, 173.34; IR (neat): 3517, 2925, 2855, 1737, 1449, 1252, 1143, 731 cm^{-1}. Anal. calcd for $C_{19}H_{29}ClO_3$: C, 66.94; H, 8.57. Found: C, 66.98; H, 8.61. (*S*,*R*)-(±)-**3b**; white solid, mp: 50–51°C (from hexane), R_f=0.25 (hexane/EtOAc=2/1); ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.89 (t, *J*=6.4 Hz, 3H), 1.28–2.05 (m, 16H), 3.78 (s, 1H), 3.82 (s, 3H), 4.61 (dd, *J*=1.6, 10.8 Hz, 1H), 7.36–7.66 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.09, 22.65, 26.85, 28.86, 29.28, 29.36, 29.48, 31.85, 33.13, 53.64, 67.54, 81.31, 125.77, 128.17, 128.31, 139.37, 172.98; IR (neat): 3553, 2954, 2925, 2850, 1739, 1449, 1257, 1135, 727 cm^{-1}. Anal. calcd for $C_{19}H_{29}ClO_3$: C, 66.94; H, 8.57. Found: C, 66.98; H, 8.61.

3.3.3. Methyl (±)-2-hydroxy-2-(*p*-methylphenyl)-3-chloro-4-methylpentanoate (3c). The crude product was purified by column chromatography (hexane/ether=160/1) to give 120 mg (44.2%) of (*S*,*S*)-(±)-**3c** and 31 mg (11.7%) of (*S*,*R*)-(±)-**3c**. (*S*,*S*)-(±)-**3c**; white solid, mp: 110–111°C, R_f=0.55 (hexane/EtOAc=2/1); ^{1}H NMR (200 MHz,

$CDCl_3$) δ 0.90 (d, J=6.4 Hz, 3H), 0.96 (d, J=6.4 Hz, 3H), 1.81 (m, 1H), 2.35 (s, 3H), 3.82 (s, 3H), 3.86 (s, 1H), 4.75 (d, J=2.0 Hz, 1H), 7.19 (d, J=8.0 Hz, 2H); 7.57(d, J=8.0 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 16.80, 21.03, 22.53, 28.95, 53.67, 73.38, 82.10, 125.73, 129.23, 135.12, 138.15, 173.82; IR (KBr): 3504, 2960, 1740, 1512, 1437, 1257, 1154, 824, 762 cm^{-1}. Anal. calcd for $C_{14}H_{19}ClO_3$: C, 62.10; H, 7.07. Found: C, 61.91; H, 7.07. (*S*,*R*)-(±)-**3c**; yellow liquid, R_f=0.50 (hexane/EtOAc=2/1); ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.09 (d, J=6.4 Hz, 3H), 1.18 (d, J=6.4 Hz, 3H), 2.14 (m, 1H), 2.35 (s, 3H), 3.78 (s, 1H), 3.80 (s, 3H), 4.64 (d, J=3.0 Hz, 1H), 7.19 (d, J=8.0 Hz, 2H); 7.53 (d, J=8.0 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 18.44, 20.99, 22.33, 32.14, 53.53, 72.78, 81.60, 125.49, 128.98, 137.39, 137.93, 173.41; IR (neat): 3504, 2940, 1734, 1512, 1437, 1251, 1147, 824, 762 cm^{-1}. Anal. calcd for $C_{14}H_{19}ClO_3$: C, 62.10; H, 7.07. Found: C, 61.91; H, 7.07.

3.3.4. Methyl (±)-2-hydroxy-2-(*p*-methylphenyl)-3-chlorooctanoate (3d). The crude product was purified by column chromatography (hexane/ether=160/1) to give 150 mg (50.4%) of (*S*,*S*)-(±)-**3d** and 45 mg (15.0%) of (*S*,*R*)-(±)-**3d**. (*S*,*S*)-(±)-**3d**; yellow liquid, R_f=0.45 (hexane/ether=2/1); ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.82 (t, J=6.8 Hz, 3H), 1.17–1.75 (m, 8H), 2.35 (s, 3H), 3.82 (s, 3H), 3.91 (s, 1H), 4.67 (dd, J=2.0, 11.0 Hz, 1H), 7.18 (d, J=8.4 Hz, 2H), 7.54 (d, J=8.4 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.80, 21.04, 22.39, 26.24, 30.51, 30.87, 53.54, 68.26, 81.21, 125.79, 129.20, 134.79, 138.18, 173.57; IR (neat): 3514, 2958, 2932, 2864, 1742, 1512, 1437, 1257, 1147, 756 cm^{-1}. Anal. calcd for $C_{16}H_{23}ClO_3$: C, 64.31; H, 7.76. Found: C, 64.34; H, 8.10. (*S*,*R*)-(±)-**3d**; yellow liquid, R_f=0.30 (hexane/ether=2/1); ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.91 (t, J=6.8 Hz, 3H), 1.27–2.04 (m, 8H), 2.36 (s, 3H), 3.75 (s, 1H), 3.81 (s, 1H), 4.61 (dd, J=2.0, 11.0 Hz, 1H), 7.20 (d, J=8.2 Hz, 2H), 7.52 (d, J=8.2 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.94, 21.02, 22.39, 26.55, 31.02, 33.08, 53.56, 67.59, 81.20, 125.64, 129.04, 136.45, 138.08, 173.07; IR (neat): 3514, 2958, 2930, 2864, 1734, 1512, 1437, 1253, 1147, 756 cm^{-1}. Anal. calcd for $C_{16}H_{23}ClO_3$: C, 64.31; H, 7.76. Found: C, 64.34; H, 8.10.

3.3.5. Methyl (±)-2-hydroxy-2-(*p*-methylphenyl)-3-chlorodecanoate (3e). The crude product was purified by column chromatography (hexane/ether=160/1) to give 182 mg (55.7%) of (*S*,*S*)-(±)-**3e** and 51 mg (15.7%) of (*S*,*R*)-(±)-**3e**. (*S*,*S*)-(±)-**3e**; colorless liquid, R_f=0.28 (hexane/ether=2/1); ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.84 (t, J=6.4 Hz, 3H), 1.18–1.60 (m, 12H), 2.35 (s, 3H), 3.82 (s, 3H), 3.89 (s, 1H), 4.66 (dd, J=1.8, 11.0 Hz, 1H), 7.18 (d, J=8.2 Hz, 2H), 7.54 (d, J=8.2 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.04, 21.02, 22.57, 26.54, 28.64, 28.99, 30.51, 31.68, 53.56, 68.25, 81.22, 125.82, 129.22, 134.80, 138.19, 173.59; IR (neat): 3514, 2958, 2930, 2860, 1742, 1512, 1437, 1251, 1147, 756 cm^{-1}. Anal. calcd for $C_{18}H_{27}ClO_3$: C, 66.14; H, 8.33. Found: C, 66.20; H, 8.53. (*S*,*R*)-(±)-**3e**; colorless liquid, R_f=0.16 (hexane/ether=2/1); ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.89 (t, J=6.4 Hz, 3H), 1.28–2.03 (m, 12H), 2.35 (s, 3H), 3.74 (s, 1H), 3.81 (s, 3H), 4.61 (dd, J=1.6, 10.8 Hz, 1H), 7.20 (d, J=8.2 Hz, 2H), 7.52 (d, J=8.2 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.06, 21.04, 22.61, 26.87, 28.81, 29.01, 31.72, 33.10, 53.56, 67.60, 81.23, 125.65, 129.05, 136.47, 138.10, 173.09; IR (neat): 3514, 2958, 2930, 2860, 1734, 1514, 1437, 1249, 1143, 756 cm^{-1}. Anal. calcd for $C_{18}H_{27}ClO_3$: C, 66.14; H, 8.33. Found: C, 66.20; H, 8.53.

3.3.6. Methyl (±)-2-hydroxy-2-(*p*-methylphenyl)-3-chlorododecanoate (3f). The crude product was purified by column chromatography (hexane/ether=160/1) to give 226 mg (63.8%) of (*S*,*S*)-(±)-**3f** and 60 mg (16.9%) of (*S*,*R*)-(±)-**3f**. (*S*,*S*)-(±)-**3f**; colorless liquid, R_f=0.45 (hexane/ether=2/1); ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.87 (t, J=6.4 Hz, 3H), 1.20–1.72 (m, 16H), 2.35 (s, 3H), 3.82 (s, 3H), 3.89 (s, 1H), 4.66 (dd, J=1.8, 11.0 Hz, 1H), 7.18 (d, J=8.2 Hz, 2H), 7.54 (d, J=8.2 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.06, 21.01, 22.62, 26.52, 28.66, 29.23, 29.31, 29.42, 30.50, 31.81, 53.54, 68.25, 81.22, 125.81, 129.22, 134.81, 138.19, 173.59; IR (neat): 3514, 2928, 1742, 1512, 1458, 1255, 1147, 756 cm^{-1}. Anal. calcd for $C_{20}H_{31}ClO_3$: C, 67.68; H, 8.80. Found: C, 67.66; H, 9.11. (*S*,*R*)-(±)-**3f**; yellow liquid, R_f=0.30 (hexane/ether=2/1); ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.89 (t, J=6.4 Hz, 3H), 1.28–2.03 (m, 16H), 2.35 (s, 3H), 3.74 (s, 1H), 3.81 (s, 3H), 4.60 (dd, J=1.6, 10.8 Hz, 1H), 7.19 (d, J=8.4 Hz, 2H), 7.52 (d, J=8.4 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.08, 21.04, 22.65, 26.87, 28.86, 29.28, 29.36, 29.47, 31.85, 33.11, 53.57, 67.60, 81.22, 125.65, 129.05, 136.47, 138.09, 173.09; IR (neat): 3514, 2928, 1734, 1514, 1458, 1251, 1147, 756 cm^{-1}. Anal. calcd for $C_{20}H_{31}ClO_3$: C, 67.68; H, 8.80. Found: C, 67.66; H, 9.11.

3.3.7. Methyl (±)-2-hydroxy-2-(*p*-ethylphenyl)-3-chlorohexanoate (3g). The crude product was purified by column chromatography (hexane/ether=160/1) to give 132 mg (46.3%) of (*S*,*S*)-(±)-**3g** and 39 mg (13.8%) of (*S*,*R*)-(±)-**3g**. (*S*,*S*)-(±)-**3g**; yellow liquid, R_f=0.30 (hexane/ether=2/1); ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.82 (t, J=7.2 Hz, 3H), 1.25 (t, J=7.6 Hz, 3H), 1.21–1.72 (m, 4H), 2.66 (q, J=7.6 Hz, 2H), 3.83 (s, 3H), 3.93 (s, 1H), 4.71 (dd, J=2.0, 11.2 Hz, 1H), 7.22 (d, J=8.4 Hz, 2H); 7.58 (d, J=8.4 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.18, 15.23, 19.71, 28.35, 35.23, 53.48, 67.96, 81.22, 125.84, 127.97, 134.99, 144.41, 173.56; IR (neat): 3514, 2966, 2936, 2876,1742, 1512, 1458, 1249, 1149, 754 cm^{-1}. (*S*,*R*)-(±)-**3g**; orange liquid, R_f=0.20 (hexane/ether=2/1); ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.96 (t, J=7.0 Hz, 3H), 1.24 (t, J=7.6 Hz, 3H), 1.45–2.12 (m, 4H), 2.66 (q, J=7.6 Hz, 2H), 3.73 (s, 1H), 3.81 (s, 3H), 4.66 (dd, J=2.0, 11.2 Hz, 1H), 7.21 (d, J=8.2 Hz, 2H); 7.54 (d, J=8.2 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.38, 15.20, 20.10, 28.37, 35.22, 53.54, 67.33, 81.26, 125.71, 127.82, 136.63, 144.32, 173.07; IR (neat): 3506, 2966, 2936, 2876, 1734, 1512, 1458, 1249, 1145, 752 cm^{-1}.

3.3.8. Methyl (±)-2-hydroxy-2-(*p*-ethylphenyl)-3-chlorooctanoate (3h). The crude product was purified by column chromatography (hexane/ether=160/1) to give 161 mg (51.5%) of (*S*,*S*)-(±)-**3h** and 38 mg (12.1%) of (*S*,*R*)-(±)-**3h**. (*S*,*S*)-(±)-**3h**; yellow liquid, R_f=0.30 (hexane/ether=2/1); ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.83 (t, J=6.4 Hz, 3H), 1.24 (t, J=7.6 Hz, 3H), 1.18–1.76 (m, 8H), 2.66 (q, J=7.6 Hz, 2H), 3.82 (s, 3H), 3.91 (s, 1H), 4.68 (dd, J=1.8, 10.8 Hz, 1H), 7.21 (d, J=8.4 Hz, 2H), 7.57 (d, J=8.4 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.89, 15.28, 22.38, 26.58, 28.37, 30.51, 30.87, 53.53, 68.30, 81.23, 125.85,

127.98, 134.97, 144.34, 173.58; IR (neat): 3504, 2959, 2931, 2872, 1740, 1509, 1457, 1250, 1145, 836 cm^{-1}. Anal. calcd for $C_{17}H_{25}ClO_3$: C, 65.27; H, 8.05. Found: C, 65.51; H, 8.22. (*S*,*R*)-(±)-**3h**; yellow liquid, R_f=0.23 (hexane/ether=2/1); ^1H NMR (200 MHz, $CDCl_3$) δ 0.90 (t, *J*=6.4 Hz, 3H), 1.24 (t, *J*=7.6 Hz, 3H), 1.20–2.10 (m, 8H), 2.66 (q, *J*=7.6 Hz, 2H), 3.73 (s, 1H), 3.81 (s, 3H), 4.61 (dd, *J*=1.6, 10.8 Hz, 1H), 7.21 (d, *J*=8.4 Hz, 2H), 7.53 (d, *J*=8.4 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.97, 15.22, 22.42, 26.57, 28.37, 31.05, 33.11, 53.58, 67.65, 81.25, 125.70, 127.83, 136.63, 144.32, 173.10; IR (neat): 3512, 2962, 2934, 2864, 1734, 1514, 1458, 1253, 1143, 835, 665 cm^{-1}. Anal. calcd for $C_{17}H_{25}ClO_3$: C, 65.27; H, 8.05. Found: C, 65.51; H, 8.22.

3.3.9. Methyl (±)-2-hydroxy-2-(*p*-ethylphenyl)-3-chlorodecanoate (3i). The crude product was purified by column chromatography (hexane/ether=160/1) to give 195 mg (57.1%) of (*S*,*S*)-(±)-**3i** and 58 mg (17.1%) of (*S*,*R*)-(±)-**3i**. (*S*,*S*)-(±)-**3i**; colorless liquid, R_f=0.30 (hexane/ether=2/1); ^1H NMR (200 MHz, $CDCl_3$) δ 0.85 (t, *J*=6.4 Hz, 3H), 1.24 (t, *J*=7.6 Hz, 3H), 1.07–1.75 (m, 12H), 2.66 (q, *J*=7.6 Hz, 2H), 3.82 (s, 3H), 3.93 (s, 1H), 4.69 (dd, *J*=1.6, 10.8 Hz, 1H), 7.21 (d, *J*=8.4 Hz, 2H), 7.58 (d, *J*=8.4 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.01, 15.27, 22.56, 26.50, 28.36, 28.60, 28.95, 30.48, 31.65, 53.50, 68.25, 81.22, 125.84, 127.97, 134.98, 144.40, 173.56; IR (neat): 3513, 2955, 2928, 2857, 1733, 1511, 1457, 1245, 1140, 758 cm^{-1}. Anal. calcd for $C_{19}H_{29}ClO_3$: C, 66.94; H, 8.57. Found: C, 66.55; H, 8.86. (*S*,*R*)-(±)-**3i**; yellow liquid, R_f=0.13 (hexane/ether=2/1); ^1H NMR (200 MHz, $CDCl_3$) δ 0.89 (t, *J*=6.4 Hz, 3H), 1.24 (t, *J*=7.6 Hz, 3H), 1.20–2.03 (m, 12H), 2.66 (q, *J*=7.6 Hz, 2H), 3.74 (s, 1H), 3.81 (s, 3H), 4.61 (dd, *J*=1.6, 10.8 Hz, 1H), 7.21 (d, *J*=8.4 Hz, 2H), 7.54 (d, *J*=8.4 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.07, 15.22, 22.62, 26.87, 28.36, 28.81, 29.02, 31.72, 33.10, 53.57, 67.63, 81.24, 125.69, 127.82, 136.62, 144.30, 173.09; IR (neat): 3514, 2960, 2930, 2860, 1734, 1514, 1458, 1249, 1143, 835, 665 cm^{-1}. Anal. calcd for $C_{19}H_{29}ClO_3$: C, 66.94; H, 8.57. Found: C, 66.55; H, 8.86.

3.3.10. Methyl (±)-2-hydroxy-2-(*p*-ethylphenyl)-3-chlorododecanoate (3j). The crude product was purified by column chromatography (hexane/ether=160/1) to give 237 mg (64.2%) of (*S*,*S*)-(±)-**3j** and 63 mg (17.1%) of (*S*,*S*)-(±)-**3j**. (*S*,*S*)-(±)-**3j**; colorless liquid, R_f=0.45 (hexane/ether=2/1); ^1H NMR (200 MHz, $CDCl_3$) δ 0.87 (t, *J*=6.4 Hz, 3H), 1.24 (t, *J*=7.6 Hz, 3H), 1.21–1.78 (m, 16H), 2.66 (q, *J*=7.6 Hz, 2H), 3.82 (s, 3H), 3.92 (s, 1H), 4.68 (dd, *J*=1.8, 11.2 Hz, 1H), 7.21 (d, *J*=8.0 Hz, 2H), 7.57 (d, *J*=8.0 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.06, 15.28, 22.62, 26.52, 28.37, 28.66, 29.23, 29.31, 29.42, 30.50, 31.81, 53.52, 68.27, 81.24, 125.85, 127.98, 134.99, 144.42, 173.58; IR (neat): 3503, 2926, 2855, 1735, 1509, 1437, 1251, 1144, 837 cm^{-1}. Anal. calcd for $C_{21}H_{33}ClO_3$: C, 68.37; H, 9.02. Found: C, 68.28; H, 9.30. (*S*,*S*)-(±)-**3j**; yellow liquid, R_f=0.30 (hexane/ether=2/1); ^1H NMR (200 MHz, $CDCl_3$) δ 0.89 (t, *J*=6.4 Hz, 3H), 1.24 (t, *J*=7.6 Hz, 3H), 1.20–2.05 (m, 16H), 2.66 (q, *J*=7.6 Hz, 2H), 3.73 (s, 1H), 3.81 (s, 3H), 4.60 (dd, *J*=1.6, 10.8 Hz, 1H), 7.21 (d, *J*=8.0 Hz, 2H), 7.54 (d, *J*=8.0 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.09, 15.22, 22.66, 26.88, 28.37, 28.87, 29.29, 29.37, 29.49, 31.86, 33.12, 53.57, 67.65, 81.25, 125.71, 127.83, 136.63, 144.32, 173.09; IR (neat): 3514, 2962, 2930, 2864, 1734, 1512, 1462, 1255, 1147, 746 cm^{-1}. Anal. calcd for $C_{21}H_{33}ClO_3$: C, 68.37; H, 9.02. Found: C, 68.28; H, 9.30.

3.3.11. Methyl (±)-2-hydroxy-2-(*p*-butylphenyl)-3-chlorohexanoate (3k). The crude product was purified by column chromatography (hexane/ether=160/1) to give 158 mg (50.5%) of (*S*,*S*)-(±)-**3k** and 37 mg (11.8%) of (*S*,*R*)-(±)-**3k**. (*S*,*S*)-(±)-**3k**; yellow liquid, R_f=0.40 (hexane/ether=2/1); ^1H NMR (200 MHz, $CDCl_3$) δ 0.82 (t, *J*=7.2 Hz, 3H), 0.94 (t, *J*=6.4 Hz, 3H), 1.27–1.71 (m, 8H), 2.62 (t, *J*=7.8 Hz, 2H), 3.83 (s, 3H), 3.92 (s, 1H), 4.70 (dd, *J*=1.8, 10.8 Hz, 1H), 7.19 (d, *J*=8.4 Hz, 2H); 7.57 (d, *J*=8.4 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.18, 13.87, 19.71, 22.34, 32.55, 33.37, 35.16, 53.46, 67.91, 81.22, 125.76, 128.50, 134.95, 143.13, 173.56; IR (neat): 3510, 2955, 2857, 1737, 1510, 1437, 1246, 1144, 760 cm^{-1}. Anal. calcd for $C_{17}H_{25}ClO_3$: C, 65.27; H, 8.05. Found: C, 64.86; H, 7.98. (*S*,*R*)-(±)-**3k**; yellow liquid, R_f=0.15 (hexane/ether=2/1); ^1H NMR (200 MHz, $CDCl_3$) δ 0.93 (t, *J*=6.6 Hz, 3H), 0.96 (t, *J*=6.4 Hz, 3H), 1.24–1.65 (m, 8H), 2.61 (t, *J*=7.6 Hz, 2H), 3.72 (s, 1H), 3.82 (s, 3H), 4.61 (dd, *J*=1.8, 10.8 Hz, 1H), 7.19 (d, *J*=8.2 Hz, 2H); 7.52 (d, *J*=8.2 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.38, 13.91, 20.12, 22.39, 32.45, 33.36, 35.21, 53.53, 67.38, 81.29, 125.65, 128.36, 136.60, 143.06, 178.08; IR (neat): 3514, 2962, 2874, 1736, 1512, 1460, 1249, 1145, 754 cm^{-1}. Anal. calcd for $C_{17}H_{25}ClO_3$: C, 65.27; H, 8.05. Found: C, 64.86; H, 7.98.

3.3.12. Methyl (±)-2-hydroxy-2-(*p*-butylphenyl)-3-chlorooctanoate (3l). The crude product was purified by column chromatography (hexane/ether=160/1) to give 183 mg (53.7%) of (*S*,*S*)-(±)-**3l** and 49 mg (14.3%) of (*S*,*R*)-(±)-**3l**. (*S*,*S*)-(±)-**3l**; colorless liquid, R_f=0.40 (hexane/ether=2/1); ^1H NMR (200 MHz, $CDCl_3$) δ 0.83 (t, *J*=6.8 Hz, 3H), 0.93 (t, *J*=7.2 Hz, 3H), 1.17–1.76 (m, 12H), 2.61 (t, *J*=7.6 Hz, 2H), 3.82 (s, 3H), 3.91 (s, 1H), 4.67 (dd, *J*=1.8, 11.0 Hz, 1H), 7.18 (d, *J*=8.2 Hz, 2H), 7.56 (d, *J*=8.2 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.68, 22.34, 26.22, 29.67, 30.50, 30.84, 33.39, 35.16, 53.49, 68.30, 81.24, 125.76, 128.51, 134.94, 143.15, 173.58; IR (neat): 3513, 2955, 2929, 2859, 1737, 1510, 1437, 1250, 1145, 761 cm^{-1}. Anal. calcd for $C_{19}H_{29}ClO_3$: C, 66.94; H, 8.57. Found: C, 66.92; H, 8.66. (*S*,*R*)-(±)-**3l**; colorless liquid, R_f=0.28 (hexane/ether=2/1); ^1H NMR (200 MHz, $CDCl_3$) δ 0.91 (t, *J*=6.8 Hz, 3H), 0.93 (t, *J*=7.2 Hz, 3H), 1.26–2.17 (m, 12H), 2.61 (t, *J*=7.6 Hz, 2H), 3.74 (s, 1H), 3.81 (s, 3H), 4.60 (dd, *J*=1.2, 11.0 Hz, 1H), 7.19 (d, *J*=8.4 Hz, 2H), 7.52 (d, *J*=8.4 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.92, 13.95, 22.40, 26.57, 31.03, 33.10, 33.37, 35.20, 53.55, 67.67, 81.25, 125.62, 128.35, 136.56, 143.05, 173.09; IR (neat): 3506, 2960, 2932, 2864, 1734, 1512, 1458, 1251, 1147, 756 cm^{-1}. Anal. calcd for $C_{19}H_{29}ClO_3$: C, 66.94; H, 8.57. Found: C, 66.92; H, 8.66.

3.3.13. Methyl (±)-2-hydroxy-2-(*p*-butylphenyl)-3-chlorodecanoate (3m). The crude product was purified by column chromatography (hexane/ether=160/1) to give 220 mg (59.5%) of (*S*,*S*)-(±)-**3m** and 61 mg (16.8%) of (*S*,*R*)-(±)-**3m**. (*S*,*S*)-(±)-**3m**; yellow liquid, R_f=0.45 (hexane/ether=2/1); ^1H NMR (200 MHz, $CDCl_3$) δ 0.88 (t, *J*=6.6 Hz, 3H),

0.94 (t, J=7.2 Hz, 3H), 1.22–1.72 (m, 16H), 2.61 (t, J=7.6 Hz, 2H), 3.83 (s, 3H), 3.91 (s, 1H), 4.68 (dd, J=1.6, 10.8 Hz, 1H), 7.19 (d, J=8.0 Hz, 2H), 7.57 (d, J=8.0 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.93, 14.08, 22.40, 22.63, 26.89, 28.82, 29.03, 31.74, 33.13, 33.38, 35.22, 53.57, 67.69, 81.28, 125.63, 128.37, 136.58, 143.07, 173.10; IR (neat): 3510, 2955, 2928, 2857, 1737, 1510, 1437, 1246, 1144, 760 cm^{-1}. Anal. calcd for $C_{21}H_{33}ClO_3$: C, 68.37; H, 9.02. Found: C, 68.40; H, 9.12. (*S*,*R*)-(±)-**3m**; yellow liquid, R_f=0.30 (hexane/ether=2/1); ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.89 (t, J=6.6 Hz, 3H), 0.92 (t, J=7.2 Hz, 3H), 1.28–2.17 (m, 16H), 2.61 (t, J=7.6 Hz, 2H), 3.72 (s, 1H), 3.81 (s, 3H), 4.59 (dd, J=1.6, 10.8 Hz, 1H), 7.19 (d, J=8.4 Hz, 2H), 7.52 (d, J=8.4 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.93, 14.08, 22.40, 22.63, 26.89, 28.82, 29.03, 31.74, 33.13, 33.38, 35.22, 53.57, 67.69, 81.28, 125.63, 128.37, 136.58, 143.07, 173.10; IR (neat): 3512, 2955, 2928, 2864, 1734, 1510, 1456, 1251, 1143, 757 cm^{-1}. Anal. calcd for $C_{21}H_{33}ClO_3$: C, 68.37; H, 9.02. Found: C, 68.40; H, 9.12.

3.3.14. Methyl (±)-2-hydroxy-2-(*p*-butylphenyl)-3-chlorododecanoate (3n). The crude product was purified by column chromatography (hexane/ether=160/1) to give 267 mg (67.3%) of (*S*,*S*)-(±)-**3n** and 80 mg (20.1%) of (*S*,*R*)-(±)-**3n**. (*S*,*S*)-(±)-**3n**; yellow liquid, R_f=0.45 (hexane/ether=2/1); ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.89 (t, J=7.2 Hz, 3H), 0.92 (t, J=7.2 Hz, 3H), 1.27–2.10 (m, 20H), 2.61 (t, J=7.8 Hz, 2H), 3.72 (s, 1H), 3.81 (s, 3H), 4.59 (dd, J=1.6, 11.0 Hz, 1H), 7.19 (d, J=8.4 Hz, 2H), 7.52 (d, J=8.4 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.93, 14.09, 22.40, 22.66, 26.89, 28.87, 29.29, 29.37, 29.49, 31.86, 33.14, 35.22, 53.55, 67.69, 81.28, 125.64, 128.36, 136.59, 143.07, 173.09; IR (neat): 3513, 2957, 2926, 2858, 1736, 1508, 1457, 1249, 1144, 837 cm^{-1}. Anal. calcd for $C_{23}H_{37}ClO_3$: C, 69.59; H, 9.39. Found: C, 69.98; H, 9.53. (*S*,*R*)-(±)-**3n**; yellow liquid, R_f=0.30 (hexane/ether=2/1); ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.89 (t, J=7.2 Hz, 3H), 0.92 (t, J=7.2 Hz, 3H), 1.27–2.10 (m, 20H), 2.61 (t, J=7.8 Hz, 2H), 3.72 (s, 1H), 3.81 (s, 3H), 4.59 (dd, J=1.6, 11.0 Hz, 1H), 7.19 (d, J=8.4 Hz, 2H), 7.52 (d, J=8.4 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.93, 14.09, 22.40, 22.66, 26.89, 28.87, 29.29, 29.37, 29.49, 31.86, 33.14, 35.22, 53.55, 67.69, 81.28, 125.64, 128.36, 136.59, 143.07, 173.09; IR (neat): 3514, 2958, 2928, 2860, 1736, 1512, 1460, 1249, 1141, 758 cm^{-1}. Anal. calcd for $C_{23}H_{37}ClO_3$: C, 69.59; H, 9.39. Found: C, 69.98; H, 9.53.

3.3.15. Methyl (*S*,*S*)-(±)-2-hydroxy-2-naphtyl-3-chlorohexanoate (3o). The crude product was purified by column chromatography (hexane/ether=160/1) to give 145 mg (47.3%) of (*S*,*S*)-(±)-**3o** and 15 mg (4.9%) of (*S*,*R*)-(±)-**3o**. (*S*,*S*)-(±)-**3o**; light green liquid, R_f=0.30 (hexane/ether=2/1); ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.79 (t, J=7.2 Hz, 3H), 1.27–1.78 (m, 4H), 3.86 (s, 3H), 4.07 (s, 1H), 4.86 (dd, J=2.0, 11.0 Hz, 1H), 7.48–8.23 (m, 7H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.19, 19.74, 32.69, 53.66, 67.85, 81.51, 123.29, 125.69, 126.41, 127.47, 128.28, 128.50, 133.01, 133.05, 133.08, 173.40; IR (neat): 3506, 2962, 2876, 1738, 1510, 1437, 1241, 1139, 758 cm^{-1}. (*S*,*R*)-(±)-**3o**; yellow liquid, R_f=0.15 (hexane/ether=2/1); ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.98 (t, J=7.2 Hz, 3H), 1.52–2.17 (m, 4H), 3.83 (s, 3H), 3.88 (s, 1H), 4.77 (dd, J=2.0, 11.0 Hz, 1H), 7.45–8.16 (m, 7H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.23, 19.94, 31.09, 53.73, 67.35, 81.50, 123.32, 125.77, 126.34, 127.47, 128.18, 128.47, 132.92, 133.01, 136.68, 172.97; IR (neat): 3506, 2962, 1734, 1603, 1510, 1437, 1243, 1137, 756 cm^{-1}.

3.3.16. Methyl (*S*,*S*)-(±)-2-hydroxy-2-naphtyl-3-chlorooctanoate (3p). The crude product was purified by column chromatography (hexane/ether=160/1) to give 140 mg (41.8%) of (*S*,*S*)-(±)-**3p** and 49 mg (14.6%) of (*S*,*R*)-(±)-**3p**. (*S*,*S*)-(±)-**3p**; yellow liquid, R_f=0.35 (hexane/ether=2/1); ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.82 (t, J=6.6 Hz, 3H), 1.16–1.82 (m, 8H), 3.87 (s, 3H), 4.15 (s, 1H), 4.88 (dd, J=1.8, 11.2 Hz, 1H), 7.51–8.26 (m, 7H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.83, 22.32, 26.21, 30.60, 30.81, 53.62, 68.14, 81.48, 125.65, 126.36, 126.58, 127.43, 128.24, 128.45, 132.95, 132.99, 135.05, 173.35; IR (neat): 3508, 2958, 2862, 1742, 1510, 1437, 1263, 1139, 758 cm^{-1}. (*S*,*R*)-(±)-**3p**; yellow liquid, R_f=0.20 (hexane/ether=2/1); ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.93 (t, J=6.4 Hz, 3H), 1.30–2.16 (m, 8H), 3.83 (s, 3H), 3.92 (s, 1H), 4.78 (dd, J=1.6, 10.8 Hz, 1H), 7.48–8.17 (m, 7H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.97, 22.43, 26.57, 31.05, 33.15, 53.71, 67.31, 81.50, 123.28, 125.42, 126.28, 126.48, 127.47, 128.07, 128.48, 132.92, 132.98, 172.94; IR (neat): 3512, 2954, 2859, 1726, 1431, 1245, 1131, 758 cm^{-1}.

3.3.17. Methyl (*S*,*S*)-(±)-2-hydroxy-2-naphtyl-3-chlorodecanoate (3q). The crude product was purified by column chromatography (hexane/ether=160/1) to give 139 mg (54.7%) of (*S*,*S*)-(±)-**3q** and 47 mg (18.5%) of (*S*,*R*)-(±)-**3q**. (*S*,*S*)-(±)-**3q**; yellow liquid, R_f=0.35 (hexane/ether=2/1); ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.84 (t, J=6.4 Hz, 3H), 1.17–1.85 (m, 12H), 3.87 (s, 3H), 4.14 (s, 1H), 4.87 (dd, J=1.8, 11.2 Hz, 1H), 7.51–8.26 (m, 7H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.97, 22.49, 26.51, 28.59, 28.92, 30.62, 31.61, 53.63, 68.13, 81.49, 123.26, 125.66, 126.37, 126.59, 127.43, 128.24, 128.45, 132.97, 132.99, 135.06, 173.37; IR (neat): 3512, 2956,, 2860, 1742, 1601, 1510, 1437, 1243, 1145, 731 cm^{-1}. Anal. calcd for $C_{21}H_{27}ClO_3$: C, 69.50; H, 7.50. Found: C, 69.68; H, 7.88. (*S*,*R*)-(±)-**3q**; yellow liquid, R_f=0.20 (hexane/ether=2/1); ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.91 (t, J=6.4 Hz, 3H), 1.30–2.11 (m, 12H), 3.83 (s, 3H), 3.92 (s, 1H), 4.77 (dd, J=1.6, 11.0 Hz, 1H), 7.48–8.17 (m, 7H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.06, 22.62, 26.89, 28.84, 29.03, 31.72, 33.17, 53.69, 67.32, 81.51, 123.29, 125.42, 126.28, 126.48, 127.47, 128.07, 128.48, 132.93, 132.99, 136.70, 172.94; IR (neat): 3501, 2957, 2927, 2855, 1727, 1508, 1458, 1262, 1135, 757 cm^{-1}. Anal. calcd for $C_{21}H_{27}ClO_3$: C, 69.50; H, 7.50. Found: C, 69.68; H, 7.88.

3.3.18. Methyl (*S*,*S*)-(±)-2-hydroxy-2-naphtyl-3-chlorododecanoate (3r). The crude product was purified by column chromatography (hexane/ether=160/1) to give 256 mg (77.4%) of (*S*,*S*)-(±)-**3r** and 16 mg (4.8%) of (*S*,*R*)-(±)-**3r**. (*S*,*S*)-(±)-**3r**; yellow liquid, R_f=0.30 (hexane/ether=2/1); ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.87 (t, J=6.4 Hz, 3H), 1.18–1.85 (m, 16H), 3.87 (s, 3H), 4.12 (s, 1H), 4.86 (dd, J=1.8, 11.0 Hz, 1H), 7.50–8.25 (m, 7H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.05, 22.59, 26.52, 28.64, 29.17, 29.27, 29.38, 30.63, 31.77, 53.65, 68.13, 81.50, 123.27, 125.68, 126.38, 126.61, 127.45, 128.26, 128.47, 132.98,

133.01, 135.05, 173.38; IR (neat): 3512, 2928, 2858, 1742, 1510, 1437, 1243, 1139, 758 cm^{-1}. Anal. calcd for $C_{23}H_{31}ClO_3$: C, 70.66; H, 7.99. Found: C, 70.96; H, 8.02. (*S*,*R*)-(±)-**3r**; yellow liquid, R_f=0.15 (hexane/ether=2/1); ^1H NMR (200 MHz, $CDCl_3$) δ 0.91 (t, *J*=6.4 Hz, 3H), 1.30–2.11 (m, 16H), 3.83 (s, 3H), 3.93 (s, 1H), 4.76 (dd, *J*=1.6, 10.8 Hz, 1H), 7.48–8.17 (m, 7H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.09, 22.65, 26.89, 28.89, 29.28, 29.38, 29.48, 31.85, 33.18, 53.70, 67.32, 81.51, 123.29, 125.43, 126.28, 126.48, 127.47, 128.07, 128.48, 132.93, 132.99, 136.71, 172.94; IR (neat): 3512, 2954, 2859, 1727, 1432, 1245, 1132, 758 cm^{-1}. Anal. calcd for $C_{23}H_{31}ClO_3$: C, 70.66; H, 7.99. Found: C, 70.96; H, 8.02.

3.4. General procedure for the preparation of compounds 4

To a stirring solution of α-chloroglycidate **1′** (0.5 mmol) in CH_2Cl_2 (5 mL) was added aluminium chloride (133 mg, 1 mmol) at 0°C. The mixture was stirred for 1 h at the same temperature, then stopped by pouring water (10 mL), the aqueous layer was extracted with EtOAc, and the combined extracts were washed with saturated $NaHCO_3$ solution and brine, then dried over $MgSO_4$. Evaporation of the solvent gave a clean oil, which was further purified by column chromatography as indicated below.

3.4.1. 2-Chloro-1-hydroxy-indan-1-carboxylic acid methyl ester (4a). The crude product was purified by column chromatography (hexane/ether=100/1) to give 66 mg (63.5%) of (1*S*,2*R*)-(±)-**4a** and 30 mg (28.6%) of isomerizarion product. (1*S*,2*R*)-(±)-**4a**; white solid, mp: 90–91°C (from Et_2O), R_f=0.50 (hexane/EtOAc=2/1); ^1H NMR (300 MHz, $CDCl_3$) δ 3.31–3.48 (m, 2H), 3.78 (s, 3H), 4.45 (s, 1H), 4.52 (dd, *J*=8.1, 9.9 Hz, 1H), 7.24–7.33 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 39.60, 53.36, 65.65, 86.79, 123.49, 124.65, 127.66, 129.53, 140.04, 140.76, 172.82; IR (neat): 3504, 2956, 1725, 1437, 1228, 1121, 765 cm^{-1}. Anal. calcd for $C_{11}H_{11}ClO_3$: C, 58.29; H, 4.89. Found: C, 58.06; H, 5.14. (1*S*,2*S*)-(±)-**4a**; light yellow liquid, R_f=0.20 (hexane/EtOAc=2/1); ^1H NMR (300 MHz, $CDCl_3$) δ 3.16 (dd, *J*=8.1, 14.1 Hz, 1H), 3. 45 (dd, *J*=6.6, 14.1 Hz, 1H), 3.80 (s, 1H), 3.89 (s, 3H), 5.17 (dd, *J*=6.6, 8.1 Hz, 1H), 7.24–7.35 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 38.54, 53.40, 58.27, 94.24, 126.99, 127.38, 128.49, 128.68, 129.41, 135.47, 186.17; IR (neat): 3496, 2956, 1736, 1455, 1262, 1093, 699 cm^{-1}. Anal. calcd for $C_{11}H_{11}ClO_3$: C, 58.29; H, 4.89. Found: C, 58.06; H, 5.14.

3.4.2. 2-Chloro-1-hydroxy-1,2,3,4-tetrahydro-naphthalene-1-carboxylic acid methyl ester (4b). The crude product was purified by column chromatography (hexane/ether=400/1) to give 38 mg (31.7%) of (1*S*,2*R*)-(±)-**4b** and 59 mg (49.2%) of (1*S*,2*S*)-(±)-**4b**. (1*S*,2*R*)-(±)-**4b**; colorless liquid, R_f=0.50 (hexane/EtOAc=2/1); ^1H NMR (300 MHz, $CDCl_3$) δ 2.31–2.39 (m, 1H), 2.69–2.84 (m, 1H), 2.99–3.02 (m, 2H), 3.76 (s, 3H), 4.35 (dd, *J*=4.2, 13.2 Hz, 1H), 4.58 (s, 1H), 7.11–7.38 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 28.80, 30.49, 53.53, 64.42, 78.60, 126.74, 126.95, 128.47, 128.65, 135.33, 135.70, 173.25; IR (neat): 3502, 2954, 1736, 1493, 1435, 1263, 1128, 774 cm^{-1}. Anal. calcd for $C_{12}H_{13}ClO_3$: C, 59.88; H, 5.44. Found: C, 60.21; H, 5.40. (1*S*,2*S*)-(±)-**4b**; white solid, mp: 64–65°C (from Et_2O), R_f=0.45 (hexane/EtOAc=2/1); ^1H NMR (300 MHz, $CDCl_3$) δ 2.20–2.26 (m, 1H), 2.41–2.49 (m, 1H), 2.99–3.04 (m, 2H), 3.84 (s, 3H), 3.88 (s, 1H), 4.66 (dd, *J*=3.6, 12.6 Hz, 1H), 7.05–7.30 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.84, 29.41, 53.45, 63.14, 96.81, 126.88, 127.87, 128.92, 129.11, 134.87, 174.21; IR (neat): 3501, 2953, 1735, 1451, 1271, 1175, 778 cm^{-1}. Anal. calcd for $C_{12}H_{13}ClO_3$: C, 59.88; H, 5.44. Found: C, 60.21; H, 5.40.

3.4.3. 6-Chloro-5-hydroxy-6,7,8,9-tetrahydro-5*H*-benzocycloheptene-1-carboxylic acid methyl ester (4c). The crude product was purified by column chromatography (hexane/ether=100/1) to give 82 mg (64.1%) of (1*S*,2*S*)-(±)-**4c**. (1*S*,2*S*)-(±)-**4c**; white solid, mp: 95–96°C (from Et_2O), R_f=0.45 (hexane/EtOAc=2/1); ^1H NMR (300 MHz, $CDCl_3$) δ 1.61–1.73 (m, 1H), 1.91–2.04 (m, 1H), 2.30–2.39 (m, 1H), 2.49–2.62 (m, 1H), 2.72 (dd, *J*=8.4, 14.4 Hz, 1H), 3.19 (dd, *J*=11.4, 13.2 Hz, 1H), 3.85 (s, 1H), 3.92 (s, 3H), 4.62 (dd, *J*=4.2, 11.4 Hz, 1H), 7.06–7.21(m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.63, 34.93, 36.14, 53.08, 65.26, 84.30, 126.19, 127.98, 128.79, 131.13, 136.88, 142.89, 173.83; IR (neat): 3510, 2953, 1736, 1449, 1266, 1122, 749 cm. Anal. calcd for $C_{13}H_{15}ClO_3$: C, 61.30; H, 5.94. Found: C, 60.98; H, 5.98.

3.4.4. 2-Chloro-1-hydroxy-6-methoxy-indan-1-carboxylic acid methyl ester (4d). The crude product was purified by column chromatography (hexane/ether=100/1) to give 100 mg (66.2%) of (1*S*,2*R*)-(±)-**4d** and 31 mg (20.5%) of (1*S*,2*S*)-(±)-**4d**. (1*S*,2*R*)-(±)-**4d**; white solid, mp: 77–78°C (from Et_2O), R_f=0.40 (hexane/EtOAc=2/1); ^1H NMR (300 MHz, $CDCl_3$) δ 3.19 (dd, *J*=9.6, 15.0 Hz, 1H), 3.30 (dd, *J*=8.1, 15.0 Hz, 1H), 3.69 (s, 3H), 3.71 (s, 3H), 4.38 (s, 1H), 4.43 (dd, *J*=8.1, 9.6 Hz, 1H), 6.72 (d, *J*=2.7 Hz, 1H), 6.81 (dd, *J*=2.7, 8.4 Hz, 1H), 7.06 (d, *J*=8.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 38.86, 53.42, 55.43, 65.78, 86.88, 107.70, 116.61, 125.50, 131.83, 141.81, 159.53, 172.83; IR (neat): 3462, 2970, 1725, 1612, 1491, 1235, 1173, 816 cm^{-1}. Anal. calcd for $C_{12}H_{13}ClO_4$: C, 56.15; H, 5.10. Found: C, 56.36; H, 5.34. (1*S*,2*S*)-(±)-**4d**; white solid, mp: 69–70°C (from Et_2O), R_f=0.30 (hexane/EtOAc=2/1); ^1H NMR (300 MHz, $CDCl_3$) δ 3.22 (dd, *J*=7.8, 15.0 Hz, 1H), 3.43 (dd, *J*=6.9, 15.0 Hz, 1H), 3.61 (s, 1H), 3.79 (s, 3H), 3.85 (s, 3H), 4.88 (dd, *J*=6.9, 7.8 Hz, 1H), 6.79 (d, *J*=2.4 Hz, 1H), 6.91 (dd, *J*=2.4, 8.4 Hz, 1H), 7.17 (d, *J*=8.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 39.22, 53.44, 55.52, 63.92, 83.41, 108.88, 116.76, 125.63, 132.34, 141.50, 159.55, 172.73; IR (neat): 3514, 2982, 1733, 1616, 1504, 1255, 1158, 829 cm^{-1}. Anal. calcd for $C_{12}H_{13}ClO_4$: C, 56.15; H, 5.10. Found: C, 56.36; H, 5.34.

3.4.5. 2-Chloro-1-hydroxy-7-methoxy-1,2,3,4-tetrahydro-naphthalene-1-carboxylic acid methyl ester (4e). The crude product was purified by column chromatography (hexane/ether=100/1) to give 68 mg (35.6%) of (1*S*,2*R*)-(±)-**4e** and 110 mg (57.6%) of (1*S*,2*S*)-(±)-**4e**. (1*S*,2*R*)-(±)-**4e**; white solid, mp: 111–112°C (from Et_2O), R_f=0.40 (hexane/EtOAc=2/1); ^1H NMR (300 MHz, $CDCl_3$) δ 2.30–2.37 (m, 1H), 2.69–2.81 (m, 1H), 2.92–2.97 (m, 2H), 3.77 (s, 3H), 3.78 (s, 3H), 4.33 (dd, *J*=4.5, 13.2 Hz, 1H), 4.57 (s, 1H), 6.91 (dd, *J*=3.0, 8.4 Hz, 1H), 6.87 (d, *J*=3.0 Hz, 1H), 7.03 (d, *J*=8.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ

28.01, 30.60, 53.59, 55.34, 64.65, 78.67, 110.76, 115.67, 127.86, 129.76, 136.18, 158.34, 173.22; IR (neat): 3444, 2956, 1733, 1615, 1501, 1281, 1132, 889 cm^{-1}. Anal. calcd for $C_{13}H_{15}ClO_4$: C, 57.68; H, 5.59. Found: C, 58.00; H, 5.80. (1*S*,2*S*)-(±)-**4e**; white solid, mp: 81–82°C (from Et_2O), R_f=0.35 (hexane/EtOAc=2/1); ^1H NMR (300 MHz, $CDCl_3$) δ 2.16–2.24 (m, 1H), 2.34–2.49 (m, 1H), 2.90–2.95 (m, 2H), 3.74 (s, 3H), 3.83 (s, 3H), 3.92 (s, 1H), 4.64 (dd, *J*=3.3, 11.8 Hz, 1H), 6.57 (d, *J*=2.7 Hz, 1H), 6.84 (dd, *J*=2.7, 8.4 Hz, 1H), 7.05 (d, *J*=8.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.96, 28.54, 53.40, 55.26, 63.20, 77.28, 112.02, 115.60, 126.90, 130.08, 135.61, 158.20, 174.08; IR (neat): 3444, 2956, 1736, 1614, 1506, 1243, 1132, 816 cm^{-1}. Anal. calcd for $C_{13}H_{15}ClO_4$: C, 57.68; H, 5.59. Found: C, 58.00; H, 5.80.

3.5. General procedure for the reaction with $AlCl_3$ supported by Al_2O_3 or SiO_2

To a stirring solution of aluminium chloride (400 mg, 3 mmol) in CH_2Cl_2 (4 mL) was added Al_2O_3 or SiO_2 (6 mmol) at room temperature. After stirred for 10 min, the solution of methyl 2-chloro-2,3-epoxyalkanoate 1(1 mmol) in CH_2Cl_2 (2 mL) was added.

The mixture was stirred for 1 h, then stopped by pouring the ice (10 mL), the aqueous layer was extracted with EtOAc, and the combined extracts were washed with saturated $NaHCO_3$ solution and brine, then dried over $MgSO_4$. Evaporation of the solvent gave a clean oil, which was further purified by column chromatography.

3.6. X-Ray structure determination

The X-Ray diffraction data for crystals *syn*-**4e** and *anti*-**4e** were collected on a CAD4 Enraf-Nonius automatic diffractometer (graphite monochromator, Cu K_α radiation (1.54184 Å), $\omega/2\theta$ scan method, $\theta \leq 57.21°$). A total of 1774 (*syn*-**4e**) and 2931 (*anti*-**4e**) reflections were measured, of which 1400 and 1772 were unique with $I>3\sigma$ respectively. The stability of crystals and of experimental conditions was checked every 2 h using three control reflections, while the orientation was monitored every 200 reflections by centering two standards. No significant decay was observed. Corrections for Lorentz and polarization effects were applied, but not for absorption. The structures were solved by direct method and difference Fourier syntheses using SIR program[12] and MolEN package.[13] All non-hydrogen atoms were refined anisotropically, H-atoms were located in δ*F* maps and refined isotropically. All figures were made using the program PLATON.[14]

Crystallographic data (excluding structure factors) for the structures *syn*-**4e** and *anti*-**4e** in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 200326 (for *syn*-**4e**) and 200327 (for *anti*-**4e**) respectively. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(0) 1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

*Crystallographic data for syn-**4e***. $C_{13}H_{15}O_3Cl$, colorless shapeless crystal of dimension 0.6×0.6×0.3mm^3, mol. weigth 254.72, monoclinic, $P2_1/n$, a=8.033(8), b=8.511(4), c=19.13(3) Å, β=99.20(6)°, V=1291 $Å^3$, Z=4, ρ=1.31 g cm^{-3}. Final R=0.046, R_w=0.061 for 1400 reflections with $I>3\sigma(I)$.

*Crystallographic data for anti-**4e***. $C_{13}H_{15}O_3Cl$, colorless prismatic crystal of dimension 0.4×0.3×0.2 mm^3, mol. weigth 254.72, monoclinic, $C2/c$, a=15.146(8), b=11.46(1), c=15.65(1) Å, β=104.05(4)°, V=2635 $Å^3$, Z=8, ρ=1.28 g cm^{-3}. Final R=0.048, R_w=0.061 for 1772 reflections with $I>3\sigma(I)$.

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