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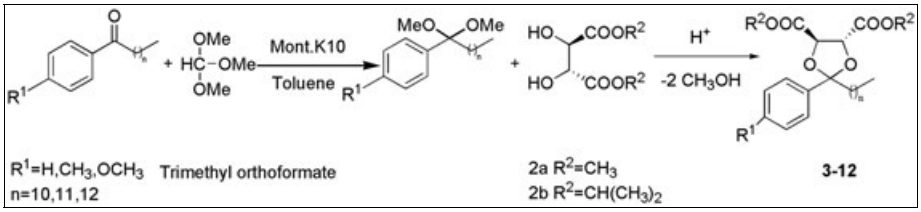

A series of chiral 1,3-dioxolanes, **3**–**12**, with >99% ee values, have been synthesized. This is the first study of chiral ketalization reaction starting from ketones with aryl, monosubstituted aryl, and long alkyl chains (C_{11}—AC_{13}). Their *ee* values were determined by chiral high-performance liquid chromatography (HPLC) on Chiralcel OD column, using their racemic 1,3-dioxolanes rac-**3**–**12**, which were also synthesized for the first time. These chiral and racemic 1,3-dioxolanes were characterizated by infrared, NMR (^{1}H, ^{13}C), mass spectrometry, elemental analysis, optical rotation, and chiral HPLC.

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INTRODUCTION

Compounds with 1,3-dioxolane's structure are of interest in the industry for the preparation of many pharmaceuticals and fragrances [1]. They are also appreciated as starting chiral pools for the synthesis of different natural compounds, like in the synthesis of (*R*)-muscone, which was synthesized using a chiral cyclic acetal [2].

1,3-Dioxolane structures have been described as chiral inhibitors of leukotrienes, which are a family of important biological molecules. 2-Acetylnaphtalene derivatives with a dioxolane structure were screened for their anticonvulsant activities. Similarly, isatin and its derivatives having dioxolane moieties exert pharmacological effects on the central nervous system, including anxiogenic, sedative, and anticonvulsant activities. Some cyclic ketals resulted from a cineole ketone were submitted to antimicrobial assays and showed their activity against several microorganisms [3].

The most convenient and practical method for the preparation of acetals is the reaction of carbonyl compounds with 1,2-diols in the presence of an acid catalyst. The catalysts commonly used are sulfuric acid, hydrocloric acid, phosphoric acid, and *p*-toluenesulfonic acid. These catalysts are often corrosive, difficult to work-up, and are not environmentally friendly [4].

In this study, montmorillonite K10-catalyst was used, which is of strong acidity and inexpensive, exposing mild reaction conditions, selectivity, easily set- and work-up possibility, and giving high yields [5]. Before using the catalyst Mont.K10, other catalysts such as *p*-toluenesulfonic acid and Amberlyst 15 were tried. Mont.K10 was found to be the best catalyst resulting in the formation of 1,3-dioxolanes from ketones with aryl, monosubstituted aryl, and long alkyl chains (C_{11}—C_{13}).

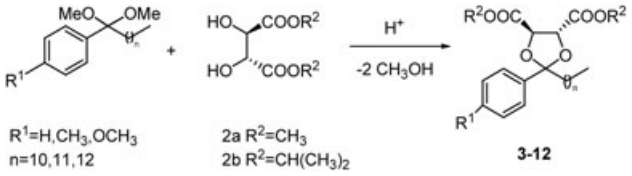
According to literature search, Mont.K10 catalyzes the formation of 1,3-dioxolanes from a various of aldehydes with ethane-1,2-diol. The sterically hindered ketones, however, failed to react with diols under same reaction conditions. Several 1,3-dioxolanes have been prepared using cyclic and aliphatic ketones with short chain lengths and benzylic ketones in the presence of Mont. K10 as an acidic catalyst [6].

However, chiral 1,3-dioxolanes with long alkyl chain lengths are missing from the literature. Therefore, the aim of this work was to synthesize chiral 1,3-dioxolanes with aryl, monosubstituted aryl, and long alkyl chain groups (C_{11}—C_{13}). Ketones **1a**–**e** with aryl, monosubstituted aryl, and long alkyl chains (C_{11}—C_{13}) were used for chiral ketalization reaction applied in this study. The ketones **1d** and **1e** are original. (*R*,*R*)-Diisopropyl-L-tartrate, (*R*,*R*)-dimethyl-L-tartrate, and montmorillonite K-10 were the other reagents, and the reaction took place under the conditions described in the experimental part.

Ten different chiral (4*R*,5*R*)-1,3-dioxolanes **3**–**12** were synthesized as original 1,3-dioxolanes for the first time in this study (Table 1). Their racemic dioxolane compounds rac-**3**–**12** have not been reported in the literature, therefore they were obtained as original racemic dioxolanes rac-**3**–**12** by ketalization of the ketones mentioned

Table 1

Ketalization of orthoesters with chiral diols (**2a,2b**) by montmorillonite K10 catalyst.[a]

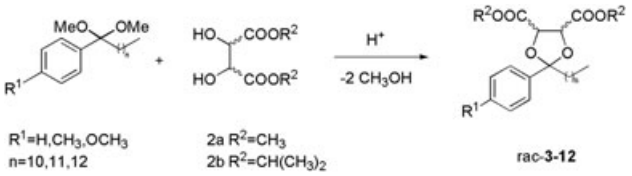


Entry	Ketone	Diol	Product	*ee*[b] (%)	Yield[c] (%)
1	**1a**	**2a**	**3**	>99	82
2	**1a**	**2b**	**4**	>99	75
3	**1b**	**2a**	**5**	>99	80
4	**1b**	**2b**	**6**	>99	77
5	**1c**	**2a**	**7**	>99	84
6	**1c**	**2b**	**8**	>99	75
7	**1d**	**2a**	**9**	>99	84
8	**1d**	**2b**	**10**	>99	75
9	**1e**	**2a**	**11**	>99	68
10	**1e**	**2b**	**12**	>99	65

[a]All reactions were carried out under Dean-Stark conditions.
[b]The enantiomeric excesses were determined by HPLC using a Chiralcel OD column. The separation conditions were given in experimental part.
[c]Isolated yield.

Table 2

Ketalization of orthoesters with racemic diols (**2c,2d**) by montmorillonite K10 catalyst.[a]



Entry	Ketone	Diol	Product	$(t_R^R)^b$ (min)	$(t_R^S)^b$ (min)	Yield[c] (%)
1	**1a**	**2c**	rac-**3**	4.225	4.965	85
2	**1a**	**2d**	rac-**4**	4.210	6.010	77
3	**1b**	**2c**	rac-**5**	4.331	6.091	82
4	**1b**	**2d**	rac-**6**	4.370	5.270	79
5	**1c**	**2c**	rac-**7**	4.160	5.420	85
6	**1c**	**2d**	rac-**8**	4.540	6.210	77
7	**1d**	**2c**	rac-**9**	5.327	6.377	87
8	**1d**	**2d**	rac-**10**	5.650	6.880	76
9	**1e**	**2c**	rac-**11**	5.400	6.930	70
10	**1e**	**2d**	rac-**12**	5.620	7.320	68

[a]All reactions were carried out under Dean-Stark conditions.
[b]The retention times were determined by HPLC using a Chiralcel OD column. Entries 1–6: mobile phase *iso*-PrOH/hexane: 5/95. Entries 7–10: mobile phase *iso*-PrOH/hexane: 3/97.
[c]Isolated yield.

above with racemic dimethyl tartrate (**2c**) and racemic diisopropyl tartrate (**2d**), respectively (Table 2). These 10 racemic 1,3-dioxolanes were used for enantioseperation and %*ee* analysis by chiral high-performance liquid chromatography (HPLC) on Chiralcel OD column, which was made also for the first time.

RESULTS AND DISCUSSION

In the first step of our study, five prochiral alkyl phenyl ketones **1a–e** were synthesized via Friedel Crafts reaction (Scheme 1) [7]. Two of them (**1d** and **1e**) were obtained for the first time in this study.

Initial attempts to ketalize ketones **1a–e** directly with diols (**2a**,**2b**) had no success. Therefore, these sterically hindered ketones **1a–e** were activated by trimethyl orthoformate (TMOF) by converting them to their more reactive orthoesters (Scheme 2). These orthoesters gave, then, the asymmetric ketalization reaction with chiral (**2a**,**2b**) and racemic diols (**2c**,**2d**) successfully with good yields and high enantiomeric excesses (>99% *ee*). In this activated ketalization reaction, methanol was separated instead of water and easy azeotropic removal of methanol, formed during the reaction, would force the equilibrium toward the cyclization products. In the literature, TMOF has been added only in some cases as additive [2,8], but the effect of TMOF has not been explained. This work demonstrates the importance of TMOF for sterically hindered ketones.

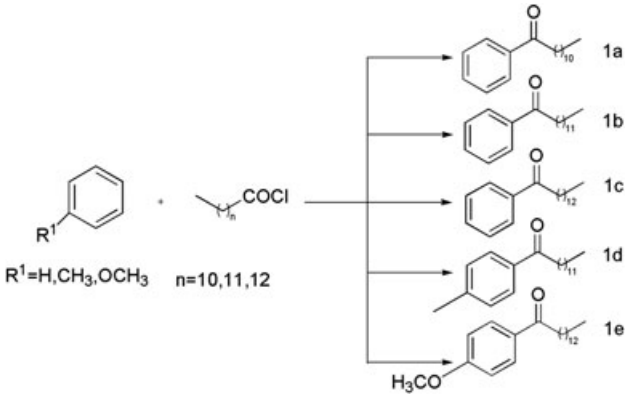
Chiral dioxolanes **3–12** (Table 1) were obtained by the reaction of orthoesters with chiral diols (**2a**,**2b**) using Mont.K10 catalyst.

Racemic dioxolanes rac-**3–12** (Table 2) were synthesized by the reaction of orthoesters with racemic diols (**2c**,**2d**) in the presence of Mont.K10 catalyst.

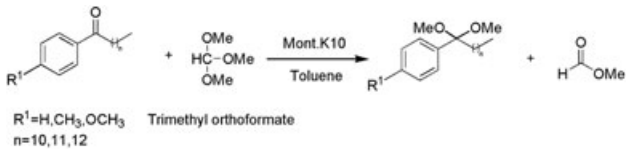
CONCLUSIONS

Ketalization was more difficult for sterically hindered ketones **1a–e** used in this study. The key step of the asymmetric ketalization strategy was solved in this study by adding TMOF. Direct ketalization did not work for long chain ketone substrates, we discovered that TMOF can

Scheme 1. Synthesis of prochiral alkyl phenyl ketones (**1a–e**).



Scheme 2. Reaction of ketones with TMOF.



catalyze the reaction and make it work. In this way, the 10 new enantiopure 1,3-dioxolanes **3**–**12** and the 10 new racemic 1,3-dioxolanes rac-**3**–**12** with long alkyl chains could be synthesized with high enantiomeric excesses and yields. The (4*R*,5*R*)- and (4*S*,5*S*)-enantiomers of 1,3-dioxolanes has not been resolved before in the literature, and therefore, racemic 1,3-dioxolanes were enantioseparated on chiral HPLC. The (*S*,*S*)-enantiomers came later than the (*R,R*)-enantiomers with changing retention time values (Table 2).

In this study, the ketalization reaction was started with enantiopure (*R*,*R*)-diols, and therefore, the products were enantiopure and of (*R*,*R*)-configuration because the two chiral centers are not directly involved in the reactions. The (*R*,*R*)-configuration of chiral 1,3-dioxolanes was checked once again by comparing the retention times of (*R*,*R*)- and (*S*,*S*)-enantiomers of racemic 1,3-dioxolanes, which were resolved on chiral HPLC.

These compounds can be used as chiral building blocks and starting materials for natural, cosmetic, and pharmaceutical purposes as seen in the synthesis of (*R*)-muscone [2]. In subsequent study, we plan to examine their possible pharmacological activities.

EXPERIMENTAL

All reagents (materials) were obtained from commercial suppliers and used as provided without further purification. Toluene was dried over sodium. The reactions were monitored with a thin layer chromatography (TLC) plate (Merck 60 F-254). Column chromatography was performed on silica gel 60 (70–230 mesh). ^{1}H- and ^{13}C-NMR spectra were measured in $CDCl_3$ and recorded on a Varian (400 MHz) Spectrometer with tetramethylsilane (TMS) as the internal standard. Mass spectra (electrospray ionization (ESI)) were recorded on Thermo Finnigen Spectrometer. Infrared (IR) spectra were recorded on a Mattson 1000 series spectrometer as thin films between NaCl plates. Optical rotations were measured on a Optical Activity AA-55 digital polarimeter and were average of more than five measurements. Enantiomeric purities of 1,3-dioxolanes were determined by chiral HPLC analyses. HPLC analysis was carried out using a Daicel CHIRALCEL OD column with a Schimatzu system.

General procedure for the synthesis of 1,3-dioxolanes (3–12 and rac-3–12). A mixture of ketone (1.0 mmol), trimethylorthoformate (0.11 mL, 1.0 mmol), Montmorillonite K-10 (300 mg), and sodium dried toluene (20.0 mL) was taken in a round-bottomed flask fitted with a Dean-Stark apparatus to stir for 1 h, then diol was added (2.0 mmol) and refluxed at 2 h (Entries 1–6)—4 h (Entries 7–10) with removing the methanol. The progress of the reaction was monitored by TLC. After cooling, the catalyst was removed by filtration. The reaction mixture was washed with solid $NaHCO_3$ and water. The organic layer was dried ($MgSO_4$) and the solvent was evaporated under reduced pressure. The colorless oil was purified by flash chromatography (silica gel, hexane/ethyl acetate as an eluent) to give 1,3-dioxolane in excellent yield.

Dimethyl (4R,5R)-2-phenyl-2-undecyl-1,3-dioxolane-4,5-dicarboxylate (3). Yield 0.344 g (82%), light yellow oil and >99% *ee*. $[\alpha]_D^{20}$ +22 (*c* 1,$CHCl_3$). IR ν_{max} (neat)/cm^{-1} 3060, 2946, 2892, 1754, 1456, 1239, 1104, 1050, 752, 725. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.31–7.48 (5H, m), 4.76–4.81 (2H, dd, *J* = 5.85 Hz), 3.83 (3H, s), 3.53 (3H, s), 1.97 (2H, t, *J* = 7.3 Hz), 1.22–1.39 (18H, m), 0.87 (3H, t, *J* = 7.3 Hz). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 168.33, 139.93, 127.2, 126.86, 124.96, 113.94, 76.34, 75.25, 51.71, 51.27, 39.72, 30.89, 28.59, 28.57, 28.52, 28.50, 28.43, 22.24, 21.65, 13.06. HPLC analysis: mobile phase ^{i}PrOH/hexane: 5/95, 35°C, flow rate: 1.0 mL/min, wavelength: 210 nm; t_R (retention time): 4.230 min. *m/z* (ESI) 420.98 [M$^+$]. Anal. calcd. for $C_{24}H_{36}O_6$: C 68.54, H 8.63. Found: C 68.43, H 8.69.

Dimethyl 2-phenyl-2-undecyl-1,3-dioxolane-4,5-dicarboxylate (rac-3). This compound was synthesized by the same aforementioned reaction of **1a** with racemic **2c**. The spectroscopic data [IR, NMR (^{1}H, ^{13}C), mass spectrometry (MS), elemental analysis] are equal to **3**.

Diisopropyl (4R,5R)-2-phenyl-2-undecyl-1,3-dioxolane-4,5-dicarboxylate (4). Yield 0.356 g (75%), light yellow oil and >99% *ee*. $[\alpha]_D^{20}$ +12 (*c* 1,$CHCl_3$). IR ν_{max} (neat)/cm^{-1} 3050, 2946, 2865, 1754, 1456, 1375, 1266, 1212, 1104, 725. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.26–7.51 (5H, m), 5.10–5.17 (1H, heptet, *J* = 6.35 Hz), 4.82–4.87 (1H, heptet, *J* = 6.35 Hz), 4.67 (2H, s), 1.97 (2H, t, *J* = 7.3 Hz), 1.29–1.30 (6H, d, *J* = 6.35 Hz), 1.22–1.27 (18H, m), 1.08–1.13 (6H, d, *J* = 6.35 Hz), 0.87 (3H, t, *J* = 7.3 Hz). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 167.44, 140.48, 127.12, 126.85, 125.00, 113.82, 76.96, 75.71, 68.61, 68.40, 39.96, 30.89, 28.47, 28.30, 22.24, 21.65, 20.69, 20.66, 20.54, 20.37, 13.07. HPLC analysis: mobile phase ^{i}PrOH/hexane: 5/95, 35°C, flow rate: 1.0 mL/min, wavelength: 210 nm; t_R (retention time): 4.190 min. *m/z* (ESI) 477.09 [M+H$^+$]. Anal. calcd. for $C_{28}H_{44}O_6$: C 70.56, H 9.19. Found: C 70.38, H 9.19.

Diisopropyl 2-phenyl-2-undecyl-1,3-dioxolane-4,5-dicarboxylate (rac-4). This compound was synthesized by the same aforementioned reaction of **1a** with racemic **2d**. The spectroscopic data [IR, NMR (^{1}H, ^{13}C), MS, elemental analysis] are equal to **4**.

Dimethyl (4R,5R)-2-phenyl-2-dodecyl-1,3-dioxolane-4,5-dicarboxylate (5). Yield 0.348 g (80%), light yellow oil and >99% *ee*. $[\alpha]_D^{20}$ +22 (*c* 1,$CHCl_3$). IR ν_{max} (neat)/cm^{-1} 3060, 2946, 2892, 1754, 1456, 1239, 1104, 1050, 752, 725. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.31–7.48 (5H, m), 4.76–4.81 (2H, dd, *J* = 5.85 Hz), 3.83 (3H, s), 3.53 (3H, s), 1.97 (2H, t, *J* = 7.3 Hz), 1.22–1.39 (20H, m), 0.87 (3H, t, *J* = 7.3 Hz). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 168.33, 139.93, 127.2, 126.86, 124.96, 113.94, 76.34, 75.25, 51.71, 51.27, 39.72, 30.89, 28.61, 28.59, 28.57, 28.52, 28.50, 28.43, 22.24, 21.65, 13.06. HPLC analysis: mobile phase ^{i}PrOH/hexane: 5/95, 35°C, flow rate: 1.0 mL/min, wavelength: 210 nm; t_R (retention time): 4.320 min. *m/z* (ESI) 434.71 [M$^+$]. Anal. calcd. for $C_{25}H_{38}O_6$: C 69.10, H 8.81. Found: C 69.06, H, 8.80.

Dimethyl 2-phenyl-2-dodecyl-1,3-dioxolane-4,5-dicarboxylate (rac-5). This compound was synthesized by the same aforementioned reaction of **1b** with racemic **2c**. The

spectroscopic data [IR, NMR (^{1}H, ^{13}C), MS, elemental analysis] are equal to **5**.

Diisopropyl (4R,5R)-2-phenyl-2-dodecyl-1,3-dioxolane-4,5-dicarboxylate (6). Yield 0.377 g (77%), light yellow oil and >99% *ee*. $[\alpha]_D^{20}$ +12 (*c* 1,$CHCl_3$). IR ν_{max} (neat)/cm^{-1} 3050, 2946, 2865, 1754, 1456, 1375, 1266, 1212, 1104, 725. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.26–7.51 (5H, m), 5.10–5.17 (1H, heptet, *J* = 6.35 Hz), 4.82–4.87 (1H, heptet, *J* = 6.35 Hz), 4.67 (2H, s), 1.97 (2H, t, *J* = 7.3 Hz), 1.29–1.30 (6H, d, *J* = 6.35 Hz), 1.22–1.27 (20H, m), 1.08–1.13 (6H, d, *J* = 6.35 Hz), 0.87 (3H, t, *J* = 7.3 Hz). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 167.44, 140.48, 127.12, 126.85, 125.00, 113.82, 76.96, 75.71, 68.61, 68.40, 39.96, 30.89, 28.57, 28.47, 28.30, 22.24, 21.65, 20.69, 20.66, 20.54, 20.37, 13.07. HPLC analysis: mobile phase ^{i}PrOH/hexane: 5/95, 35°C, flow rate: 1.0 mL/min, wavelength: 210 nm; t_R (retention time): 4.380 min. *m/z* (ESI) 490.40 [M^+]. Anal. calcd. for $C_{29}H_{46}O_6$: C 70.99, H 9.45. Found: C 70.78, H 9.44.

Diisopropyl 2-phenyl-2-dodecyl-1,3-dioxolane-4,5-dicarboxylate (rac-6). This compound was synthesized by the same aforementioned reaction of **1b** with racemic **2d**. The spectroscopic data [IR, NMR (^{1}H, ^{13}C), MS, elemental analysis] are equal to **6**.

Dimethyl (4R,5R)-2-phenyl-2-tridecyl-1,3-dioxolane-4,5-dicarboxylate (7). Yield 0.376 g (84%), light yellow oil and >99% *ee*. $[\alpha]_D^{20}$ +20 (*c* 1,$CHCl_3$). IR ν_{max} (neat)/cm^{-1} 3060, 2892, 1754, 1456, 1239, 1104, 1050, 752, 725. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.19–7.40 (5H, m), 4.69–4.74 (2H, dd, *J* = 5.85 Hz), 3.76 (3H, s), 3.46 (3H, s), 1.90 (2H, t, *J* = 7.3 Hz), 1.14–1.22 (22H, m), 0.80 (3H, t, *J* = 7.3 Hz). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 168.33, 139.91, 127.30, 126.86, 124.96, 113.93, 76.33, 75.23, 51.74, 51.29, 39.71, 30.90, 28.65, 28.62, 28.61, 28.59, 28.52, 28.50, 28.43, 28.33, 22.23, 21.66, 13.07. HPLC analysis: mobile phase ^{i}PrOH/hexane: 5/95, 35°C, flow rate: 1.0 mL/min, wavelength: 210 nm; t_R (retention time): 4.250 min. *m/z* (ESI) 449.33 [M+H^+]. Anal. calcd. for $C_{26}H_{40}O_6$: C 69.61, H 8.99. Found: C 68.35, H 8.85.

Dimethyl 2-phenyl-2-tridecyl-1,3-dioxolane-4,5-dicarboxylate (rac-7). This compound was synthesized by the same aforementioned reaction of **1c** with racemic **2c**. The spectroscopic data [IR, NMR (^{1}H, ^{13}C), MS, elemental analysis] are equal to **7**.

Diisopropyl (4R,5R)-2-phenyl-2-tridecyl-1,3-dioxolane-4,5-dicarboxylate (8). Yield 0.356 g (75%), light yellow oil and >99% *ee*. $[\alpha]_D^{20}$ +14 (*c* 1,$CHCl_3$). IR ν_{max} (neat)/cm^{-1} 3050, 2946, 2892, 1754, 1456, 1375, 1294, 1212, 1104, 752, 725. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.19–7.43 (5H, m), 5.03–5.10 (1H, heptet, *J* = 6.35 Hz), 4.74–4.81 (1H, heptet, *J* = 6.35 Hz), 4.60 (2H, s), 1.89 (2H, t, *J* = 7.3 Hz), 1.21–1.23 (6H, d, *J* = 6.35 Hz), 1.14–1.17 (22H, m), 0.99–1.06 (6H, d, *J* = 6.35 Hz), 0.80 (3H, t, *J* = 7.3 Hz). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 168.67, 141.69, 128.35, 128.07, 126.22, 115.04, 78.17, 76.91, 69.82, 69.62, 41.18, 32.13, 29.87, 29.85, 29.84, 29.82, 29.76, 29.75, 29.69, 29.55, 23.46, 22.89, 21.92, 21.59, 14.30. HPLC analysis: mobile phase ^{i}PrOH/hexane: 5/95, 35°C, flow rate: 1.0 mL/min, wavelength: 210 nm; t_R (retention time): 4.513 min. *m/z* (ESI) 505.01 [M+H^+]. Anal. calcd. for $C_{30}H_{48}O_6$: C 71.39, H 9.59. Found: C 71.22, H 9.62.

Diisopropyl 2-phenyl-2-tridecyl-1,3-dioxolane-4,5-dicarboxylate (rac-8). This compound was synthesized by the same aforementioned reaction of **1c** with racemic **2d**. The spectroscopic data [IR, NMR (^{1}H, ^{13}C), MS, elemental analysis] are equal to **8**.

Dimethyl (4R,5R)-2-(4-methylphenyl)-2-dodecyl-1,3-dioxolane-4,5-dicarboxylate (9). Yield 0.376 g (84%), light yellow oil and >99% *ee*. $[\alpha]_D^{20}$ +18 (*c* 1,$CHCl_3$). IR ν_{max} (neat)/cm^{-1} 2946, 2892, 1754, 1510, 1483, 1375, 1266, 1104, 1050, 833, 752. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.26–7.28 (2H, d, *J* = 7.8 Hz), 7.03–7.05 (2H, d, *J* = 7.8 Hz), 4.67–4.72 (2H, dd, *J* = 5.85 Hz), 3.76 (3H, s), 3.48 (3H, s), 2.25 (3H, s), 1.86 (2H, t, *J* = 7.3 Hz), 1.14–1.18 (20H, m), 0.80 (3H, t, *J* = 6.8 Hz). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 169.59, 138.22, 138.14, 128.40, 126.13, 115.26, 77.50, 76.41, 52.95, 52.52, 40.97, 29.84, 29.83, 29.76, 29.74, 29.70, 29.66, 29.63, 29.51, 23.49, 22.88, 21.32, 14.29. HPLC analysis: mobile phase ^{i}PrOH/hexane: 3/97, 35°C, flow rate: 1.0 mL/min, wavelength: 210 nm; t_R (retention time): 5.312 min. *m/z* (ESI) 471.18 [M+Na^+]. Anal. calcd. for $C_{26}H_{40}O_6$: C 69.61, H 9.59. Found: C 69.36, H 8.87.

Dimethyl 2-(4-methylphenyl)-2-dodecyl-1,3-dioxolane-4,5-dicarboxylate (rac-9). This compound was synthesized the by the same aforementioned reaction of **1d** with racemic **2c**. The spectroscopic data [IR, NMR (^{1}H, ^{13}C), MS, elemental analysis] are equal to **9**.

Diisopropyl (4R,5R)-2-(4-methylphenyl)-2-dodecyl-1,3-dioxolane-4,5- dicarboxylate (10). Yield 0.356 g (75%), light yellow oil and >99% *ee*. $[\alpha]_D^{20}$ +14 (*c* 1,$CHCl_3$). IR ν_{max} (neat)/cm^{-1} 2946, 2892, 1754, 1456, 1239, 1104, 1050, 833, 752. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.30–7.31 (2H, d, *J* = 8.3 Hz), 7.03–7.04 (2H, d, *J* = 8.3 Hz), 4.03–5.10 (1H, heptet, *J* = 6.35 Hz), 4.76–4.90 (1H, heptet, *J* = 6.35 Hz), 4.58 (2H, s), 2.24 (3H, s), 1.88 (2H, t, *J* = 7.3 Hz), 1.21–1.22 (6H, d, *J* = 6.35 Hz), 1.14–1.16 (20H, m), 1.01–1.07 (6H, d, *J* = 6.35 Hz), 0.80 (3H, t, *J* = 7.3 Hz). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 168.71, 138.73, 138.02, 128.75, 126.17, 115.13, 78.12, 76.87, 69.78, 69.59, 41.18, 32.12, 29.84, 29.83, 29.80, 29.78, 29.76, 29.70, 29.55, 23.49, 22.89, 21.92, 21.60, 21.30, 14.30. HPLC analysis: mobile phase ^{i}PrOH /hexane: 3/97, 35°C, flow rate: 1.0 mL/min, wavelength: 210 nm; t_R (retention time): 5.628 min. *m/z* (ESI) 505.37 [M+H^+]. Anal. calcd. for $C_{30}H_{48}O_6$: C 71.39, H 9.59. Found: C 71.42, H 9.33.

Diisopropyl 2-(4-methylphenyl)-2-dodecyl-1,3-dioxolane-4,5-dicarboxylate (rac-10). This compound was synthesized by the same aforementioned reaction of **1d** with racemic **2d**. The spectroscopic data [IR, NMR (^{1}H, ^{13}C), MS, elemental analysis] are equal to **10**.

Dimethyl (4R,5R)-2-(4-methoxyphenyl)-2-tridecyl-1,3-dioxolane-4,5- dicarboxylate (11). Yield 0.325 g (68%), light yellow oil and >99% *ee*. $[\alpha]_D^{20}$ +18 (*c* 1,$CHCl_3$). IR ν_{max} (neat)/cm^{-1} 2946, 2892, 1754, 1537, 1456, 1266, 1212, 1104, 1050, 833, 779. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.30–7.31 (2H, d, *J* = 7.8 Hz), 6.75–6.76 (2H, d, *J* = 7.8 Hz), 4.67–4.74 (2H, dd, *J* = 5.85 Hz), 3.76 (3H, s), 3.72 (3H, s), 3.49 (3H, s), 1.88 (2H, t, *J* = 6.84 Hz), 1.14–1.23 (22H, m), 0.80 (3H, t, *J* = 7.3 Hz). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 168.41, 158.57, 131.99, 130.58, 126.33, 112.20, 76.27, 75.17, 51.73, 51.34, 39.80, 30.90, 28.69, 28.66, 28.62, 28.60, 28.54, 28.51, 28.45, 28.33, 22.32, 21.66, 14.10. HPLC analysis: mobile phase ^{i}PrOH/hexane: 3/97, 35°C, flow rate: 1.0 mL/min, wavelength: 210 nm; t_R (retention time): 5.440 min. *m/z* (ESI) 479.25 [M+H^+]. Anal. calcd. for $C_{27}H_{42}O_7$: C 67.76, H 8.84. Found: C 67.72, H 8.61.

Dimethyl 2-(4-methoxyphenyl)-2-tridecyl-1,3-dioxolane-4,5-dicarboxylate (rac-11). This compound was synthesized by the same aforementioned reaction of **1e** with racemic **2c**. The spectroscopic data [IR, NMR (^{1}H, ^{13}C), MS, elemental analysis] are equal to **11**.

Diisopropyl (4R,5R)-2-(4-methoxyphenyl)-2-tridecyl-1,3-dioxolane-4,5- dicarboxylate (12). Yield 0.347 g (65%), light yellow oil and >99% *ee*. $[\alpha]_D^{20}$ +14 (*c* 1,$CHCl_3$). IR ν_{max} (neat)/cm^{-1} 2973, 2892, 1754, 1619, 1510, 1483, 1375, 1266, 1104, 1050, 833, 779. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.33–7.35 (2H, d, *J* = 8.3 Hz), 6.75–6.76 (2H, d, *J* = 8.3 Hz), 5.04–5.09 (1H, heptet, *J* = 6.35 Hz), 4.77–4.82 (1H, heptet, *J* = 6.35 Hz), 4.58 (2H, s), 3.71 (3H, s), 1.88 (2H, t, *J* = 7.3 Hz), 1.21–1.23 (6H, d, *J* = 6.35 Hz), 1.14–1.16 (22H, m), 1.03–1.04 (6H, d, *J* = 5.86 Hz), 0.80 (3H, t, *J* = 7.3 Hz). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 168.73, 159.73, 133.87, 132.95, 127.57, 113.41, 78.11, 76.88, 69.79, 69.61, 55.43, 41.24, 32.13, 29.88, 29.86, 29.84, 29.83, 29.78, 29.75, 29.71, 29.55, 23.54, 22.88, 21.92, 21.67, 14.29. HPLC analysis: mobile phase ^{i}PrOH/hexane: 3/97, 35°C, flow rate: 1.0 mL/min, wavelength: 210 nm; t_R (retention time): 5.770 min. *m/z* (ESI) 535.65 [M^+]. Anal. calcd. for $C_{31}H_{50}O_7$: C 69.63, H 9.42. Found: C 69.59, H 9.41.

Diisopropyl 2-(4-methoxyphenyl)-2-tridecyl-1,3-dioxolane-4,5-dicarboxylate (rac-12). This compound was synthesized by the same aforementioned reaction of **1e** with racemic **2d**. The spectroscopic data [IR, NMR (^{1}H, ^{13}C), MS, elemental analysis] are equal to **12**.

SUPPORTING INFORMATION

IR, ^{1}H NMR, and ^{13}C NMR spectra are available.

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