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Synthesis and structure of titanium alkoxide complexes with bulky ligands derived from natural products Asymmetric epoxidation of cinnamyl alcohol

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Abstract

A family of titanium(IV) alkoxide compounds [{Ti(OPr^i)$_3$(OR)}$_2$], [{Ti(OPr^i)$_2$(OR)$_2$}$_2$], and Ti(OR)$_4$ (**1**–**12**) have been prepared using two different routes: by metathesis reaction of TiCl(OPr^i)$_3$ and TiCl$_2$(OPr^i)$_2$ with ROH in the presence of Et$_3$N and alternatively by alcohol exchange of Ti(OPr^i)$_4$ and the corresponding higher boiling alcohol (ROH = adamantanol, 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose, 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose, 1*R*,2*S*,5*R*-(−)-menthol). These tetra alkoxide titanium(IV) compounds have been characterized by spectroscopic techniques. In addition, some of these chiral Lewis acid titanium compounds, derived from diacetone galactose and diacetone glucose, have been studied in the asymmetric epoxidation of cinnamyl alcohol in order to evaluate their catalytic activity and stereoselectivity.

Keywords: Titanium; Alkoxide; Carbohydrates; Asymmetric epoxidation

1. Introduction

Over the past two decades the use of titanium complexes containing alkoxide ligands as reagents and catalysts for organic synthesis has undergone a rapid expansion. Titanium alkoxide reagents have been used as catalysts for enantioselective addition of nucleophiles to carbonyl groups [1], alkynylation of aldehydes [2], polymerization of olefins [3], and widely in the epoxidation of allylic alcohols especially since the discovery of asymmetric epoxidation in 1980 by Sharpless and coworker [4].

Sharpless epoxidation using Ti(OPr^i)$_4$ in the presence of *tert*-butylhydroperoxide and a chiral tartrate ligand converts an allylic alcohol into epoxides with good yield and excellent enantioselectivity. Although this catalytic process seems to be well understood, it is clear that the chiral ligand is critical in enantioselectivity [5]. The complexity of titanium alkoxide coordination chemistry has often contributed to a substantial degree of uncertainty in the identity of the catalytically active species in these systems.

The solution state of most Ti(OR)$_4$ (R = Me, Et, Bu^n) appears to be an equilibrium between mono-, di-, and trinuclear species, favoring the trinuclear species at room temperature. When the steric bulk of the alkoxide is increased (OR = OPr^i, OBu^t) monomeric species are reported. Ti(OPr^i)$_4$, the most investigated and utilized titanium alkoxide, is an oil and has an aggregation of 1.4, indicating some degree of oligomerization in solution [6]. Ti(ONp)$_4$ (ONp = OCH$_2$CMe$_3$) has been structurally characterized and adopts a typical Ti$_2$(μ-ONp)$_2$(ONp)$_6$ structure widely observed for other metal alkoxides [7].

Sugars can be used to assemble transition metal complexes in novel structures. The molecules thus

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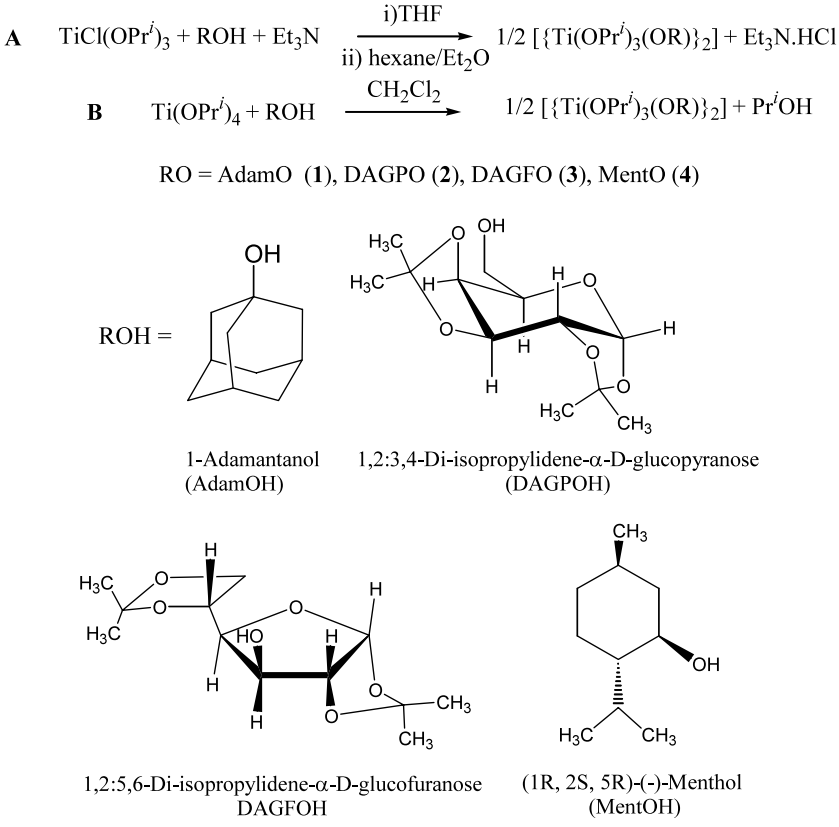
formed take advantage of the intrinsic properties of both sugars and metal. Sugars are natural chiral ligands and sugar metal complexes should therefore have pronounced three-dimensional characteristics like receptor cavities. These complexes also provide different chemistry from the habitual [8]. For these purposes we have used in our work the monosaccharides 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose and 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose previously used by Floriani and coworkers [9].

In this paper, we report the synthesis of [{Ti(O-Pr^i)$_3$(OR)}$_2$], [{Ti(OPr^i)$_2$(OR)$_2$}$_2$], and Ti(OR)$_4$ (RO = adamantanoxi (AdamO), 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranoxi (DAGPO), 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranoxi (DAGFO), and 1*R*,2*S*,5*R*-(−)-menthoxi (MentO)). The main characteristic of this family of titanium(IV) bulky alkoxide compounds is that these chiral ligands are derived from natural products. In all cases the ligands are commercially available. In addition, the study of these new compounds in the asymmetric epoxidation of cinnamyl alcohol has been developed as test reactions in order to evaluate the catalytic activity of these new titanium(IV) alkoxide complexes.

2. Results and discussion

The titanium alkoxides Ti(OPr^i)$_{4-n}$(OAdam)$_n$ ($n = 1$ (**1**), $n = 2$ (**5**), $n = 4$ (**9**)), Ti(OPr^i)$_{4-n}$(ODAGP)$_n$ ($n = 1$ (**2**), $n = 2$ (**6**), $n = 4$ (**10**)), Ti(OPr^i)$_{4-n}$(ODAGF)$_n$ ($n = 1$ (**3**), $n = 2$ (**7**), $n = 4$ (**11**)), and Ti(OPr^i)$_{4-n}$(OMent)$_n$ ($n = 1$ (**4**), $n = 2$ (**8**), $n = 4$ (**12**)) have been prepared using two general strategies: reaction of TiCl(OPr^i)$_3$ and TiCl$_2$(OPr^i)$_2$ with the appropriate amount of alcohol in the presence of triethylamine using THF as solvent (procedure A) and reaction of Ti(OPr^i)$_4$ with the corresponding stoichiometric amount of alcohol to release one, two, or four equivalents of Pr^{i}OH (procedure B) as shown in Eqs. (1) and (2).



(1)

When $n = 1$ the products are isolated as white solids or colorless crystals. When $n = 2$ or 4 white solids or colorless oils are isolated. All compounds are soluble in common organic solvents and are extremely moisture-sensitive.

Compounds **1**–**12** have been characterized by IR, ^{1}H-, and ^{13}C-NMR spectroscopy. ^{1}H- and ^{13}C-NMR spectra of the isolated compounds indicate that the desired

$$\mathbf{A}\ \ TiCl_2(OPr^i)_2 + 2\ ROH + 2\ Et_3N \xrightarrow[\text{ii) hexane/}Et_2O]{\text{i)THF}} 1/2\ [\{Ti(OPr^i)_2(OR)_2\}_2] + 2\ Et_3N.HCl$$

$$\mathbf{B}\ \ Ti(OPr^i)_4 + 2\ ROH \xrightarrow{CH_2Cl_2} 1/2\ [\{Ti(OR)_2(OPr^i)_2\}_2] + 2\ Pr^iOH$$

RO = AdamO (**5**), DAGPO (**6**), DAGFO (**7**), MentO (**8**) (2)

$$\mathbf{B}\ \ Ti(OPr^i)_4 + 4\ ROH \xrightarrow{CH_2Cl_2} Ti(OR)_4 + 4\ Pr^iOH$$

RO = AdamO (**9**), DAGPO (**10**), DAGFO (**11**), MentO (**12**)

alcoholysis exchange or metathesis reaction has taken place cleanly. In the ^{1}H-NMR spectra, as n is increased there is an increase in the integral of the signals associated with the bulky alkoxide ligands and a decrease of the integrals of the isopropoxide signals.

The solution ^{1}H-NMR spectra of $Ti(OPr^i)_{4-n}(OR)_n$ ($n = 1$, 2, and 4) (**1**–**12**) are straightforward with only signal for the isopropoxide group and a single set of resonances for the corresponding bulky alkoxide ligand indicating the presence of only one type of isopropoxide ligands and showing the bulky ligands to be equivalent. These spectra are consistent with a mononuclear compound or a polynuclear species that is exhibiting rapid dynamic exchange between bridging and terminal alkoxide ligands [6].

^{1}H-NMR spectra of compounds $Ti(OPr^i)_{4-n}(OAdam)_n$ ($n = 1$ (**1**), $n = 2$ (**5**), $n = 4$ (**9**)), synthesized as models of alkoxide complexes with a steric demanding ligand [10,11], show in the range $\delta =$ 1.57–1.59, 1.78–1.81, and 2.09–2.12 ppm the signals corresponding to the protons H_δ, H_β, and H_γ, respectively (see Fig. 1(a) for **1**), and for compounds **1** and **5** sharp signals for the septuplet of the methyne group of the isopropoxide ligand at $\delta = 4.47$ and 4.48 ppm, respectively.

^{1}H-NMR spectra of compounds $Ti(OPr^i)_{4-n}(ODAGP)_n$ ($n = 1$ (**2**), $n = 2$ (**6**), $n = 4$ (**10**)) have been recorded at room temperature in $CDCl_3$ and different decoupling NMR experiments allowed us to identify the signals and calculate the corresponding coupling constants. The diacetone galactopyranose monoanion binds as a terminal alkoxy ligand to the titanium center. Compound **2** shows in its spectrum at $\delta = 1.22$ ppm a doublet assigned to the methyl groups and at $\delta = 4.47$ ppm a well-resolved septuplet for the methyne group of the isopropoxide ligand. At $\delta = 1.30$, 1.32, 1.42, and 1.52 ppm four singlet signals corresponding to the non-equivalent methyl groups of the diacetone galactopyranose ligand were also observed (see Fig. 1(b)). The anomeric proton H1 appears as a doublet at

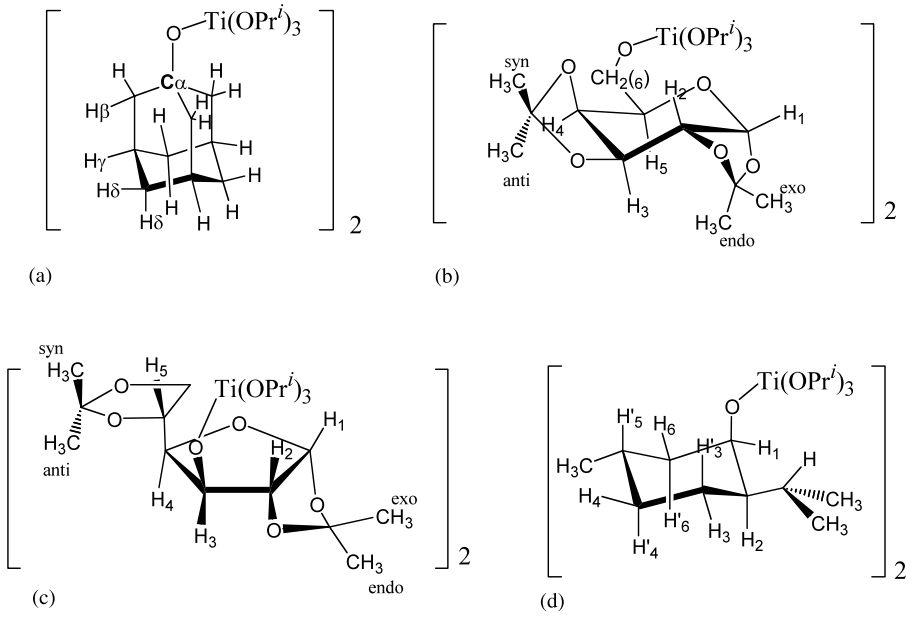


Fig. 1. Representation of compounds **1**–**4** showing the hydrogen atom labelling scheme.

$\delta = 5.48$ ppm. ^{1}H-NMR spectra for compounds **6** and **10** show a similar pattern of signals for the diacetone galactopyranose ligands.

The coupling constants in **2**, **6**, and **10**, $^3J_{H1-H2}$ (4.8 Hz), between the anomeric H1 and the H2 are consistent with the *cis* disposition of these protons in the protected galactopyranose ligand. The rest of the coupling constants $^3J_{HH}$ in the sugar ring are values typical for pyranoside ring systems [12].

^{1}H-NMR spectrum of compound **3** shows well-resolved signals, a doublet at $\delta = 1.21$ ppm and a septuplet at $\delta = 4.47$ ppm, assigned to the isopropoxide ligands and four singlet signals at $\delta = 1.28$, 1.32, 1.39, and 1.45 ppm for the non-equivalent methyl groups of the diacetone glucofuranose ligand. The anomeric proton H1 appears as a doublet at $\delta = 5.87$ ppm (see Fig. 1(c)). ^{1}H-NMR spectra for compounds **7** and **11** show a similar pattern of signals for the diacetone glucofuranose ligands (see Section 4).

The ^{1}H-NMR spectrum of compound **4** shows well-resolved signals, a doublet at $\delta = 1.21$ ppm, and a septuplet at $\delta = 4.45$ ppm, assigned to the isopropoxide ligands and the expected signals for the menthol ligand (see Fig. 1(d)). H1 appears as a multiplet at $\delta = 3.88$ ppm deshielded by nearly 0.50 ppm with respect to the free ligand (see Section 4). Similar ^{1}H-NMR spectra were found for complexes **8** and **12**. A chlorotitanate

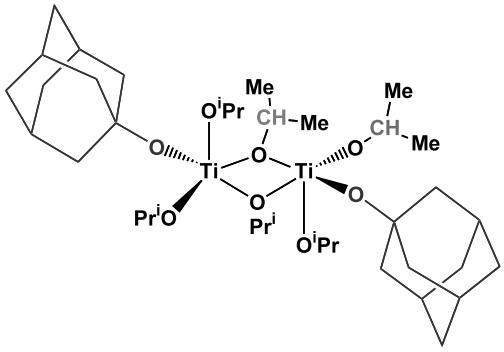


Fig. 3. Proposed structure for [{Ti(OPr^i)$_3$(OAdam)}$_2$]

family of compounds bearing menthol ligand used for enantioselective addition to aldehydes has been published previously by Seebach and coworkers [13].

Titanium has a tendency to coordinately saturate its binding sphere unless a large number of sterically hindered ligands are used. Therefore, it is probable that in some of our complexes the central core consists of an inter-linked titanium isopropoxide moiety that is protected by an outer sphere of bulky alkoxide ligands [14]. The steric bulk around the metal center inhibits oligomerization.

To elucidate the solution behavior of this family of compounds, variable temperature NMR studies of compounds **1**, **8**, and **9** as representative examples

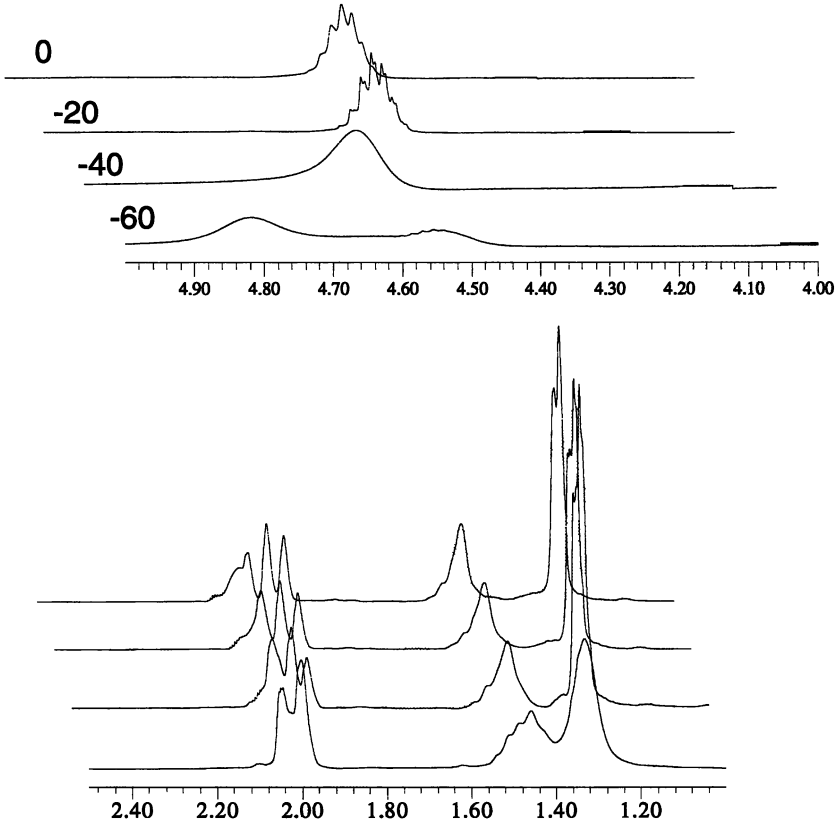


Fig. 2. Variable temperature 400 MHz ^{1}H-NMR spectrum of **1** in toluene-d$_8$.

were undertaken. ^{1}H-NMR spectrum of compound **1** in toluene shows sharp signals at room temperature; when the temperature is lowered the resonance of the methyne groups OCH become broader indicating some fluxionality in the solution-state structure. Lowering the temperature to -60 °C the resonance from OCH undergoes decoalescence to produce a pair of very broad resonances centered at $\delta = 4.4$ and 4.7 ppm. The doublet from the methyl groups broadens, although at -60 °C we were unable to observe the differentiation of the methyl groups of the two distinct isopropoxide ligands, bridging and terminal. In addition, non-significant changes are observed in the resonances corresponding to the bulky alkoxide ligand (see Fig. 2). According to the temperature-dependent NMR spectra solutions compound **1** establish a monomer–dimer equilibrium which favors the existence of the dimer. The inequivalence of the isopropoxide ligands at -60 °C is consistent with the existence of a dinuclear complex in which the two metals are joined through an alkoxide bridge adopting an edge-bridged bis(trigonal–bipyramidal) coordination environment (Fig. 3).

In a similar way, variable temperature ^{1}H-NMR study for **8** in toluene was accomplished. The spectra show well-resolved signals at room temperature, a broad resonance for the methyne group at -40 °C, and a pair of very broad resonances centered at $\delta = 4.4$ and 4.8 ppm at -60 °C. Unlike compounds **1** and **8**, compound **9** does not present any dynamical behavior in temperature range used in these experiments (room temperature to -80 °C) indicating that the complex is monomeric in solution.

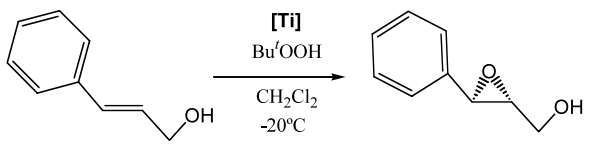
In order to gain more insight on the proposed dimeric structure in the complexes, the solid-state ^{13}C MAS-NMR spectrum of compounds [{Ti(OPr^i)$_3$(OAdam)}$_2$] (**1**) and [Ti(OAdam)$_4$] (**9**) were also recorded. Compounds **1** and **9** were chosen due to the easier pattern of signals expected for them in the range where the methyne groups of the isopropoxides should appear compared to those anticipated for other chiral ligands. In fact, the ^{13}C MAS-NMR spectrum of **1** revealed three different signals in the range $\delta = 70$–85 ppm, a strong signal at $\delta = 78.3$ ppm assigned to the C_α of the adamantanoxy ligand and two weak signals around $\delta = 75.5$ ppm that can be attributed to the methyne carbons of two different isopropoxide groups in the solid state. Compound **9** shows a very similar pattern of signals for adamantanoxy substituents at $\delta = 47.0$, 38.3, 31.8, and 78.8 ppm assigned to the C_β, C_δ, C_γ, and C_α, respectively.

To further support our proposal of the dimeric structure for lower substituted compounds, an FAB mass spectroscopic study was carried out for **6** and **8**. Peaks m/z 1368 [M$^+$] for **6** and 953 [M$^+$] for **8** were observed which indicate that **6** and **8** are dimeric species.

Some preliminary studies into the catalytic activity of some of these compounds in the asymmetric epoxidation of cinnamyl alcohol have been carried out. Cinnamyl alcohol was epoxidized at -20 °C with a catalyst/substrate/*tert*-butylhydroperoxide (Bu^{t}OOH) ratio of 1/20/40 using CH_2Cl_2 as solvent in the presence of molecular sieves, with experimental conditions similar to those used by Sharpless except the reaction time which was increased to 5 h. The yields and the enantiomeric excess values of the epoxy alcohols were determined by HPLC with a chiralpack AD-H column from VWR International Eurolab. Table 1 shows the results of the asymmetric epoxidation using compounds **6** and **7**.

The cinnamyl alcohol led with compounds **6** and **7** the (+)-(2*R*, 3*R*) epoxide as the preferred enantiomer. The asymmetric epoxidation proceeds with good yields and low enantiomeric excess as determined by HPLC.

Table 1



Catalyst	Time (h)	Yield (%)	ee (%)
[{Ti(OPr^i)$_2$(ODAGP)$_2$}$_2$] (**6**)	5	65	22
[{Ti(OPr^i)$_2$(ODAGF)$_2$}$_2$] (**7**)	5	60	17

3. Conclusions

In conclusion, a family of titanium(IV) alkoxide compounds have been prepared. In basis of solid-state NMR and NMR variable temperature studies we assume the lower substituted titanium compounds Ti(OPr^i)$_{4-n}$(OR)$_n$ ($n = 1$, 2) to be dimeric in solution and solid state meanwhile higher substituted Ti(OR)$_4$ are mononuclear due to the steric hindrance imposed by the bulky alkoxide ligands if the nuclearity is greater than 1 [15]. Compounds **6** and **7** have been tested as catalysts in the enantioselective epoxidation of cinnamyl alcohol. Further catalytic experiments are currently being studied.

4. Experimental

4.1. General remarks

All reactions were performed using standard Schlenk tube and dry box techniques under an atmosphere of dry nitrogen or argon. Solvents were distilled from appropriate drying agents and degassed before use.

1,2:3,4-Di-*O*-isopropylidene-α-D-galactopyranose, 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose, 1*R*,2*S*,5*R*-(−)-menthol, adamantanol, and $TiCl(OPr^i)_3$ (1 M hexane) were purchased from Aldrich and used as received. $Ti(OPr^i)_4$ and NEt_3 were purchased from Aldrich that were distilled and stored under an argon atmosphere prior to use. $TiCl_2(OPr^i)_2$ was prepared according to the literature procedure [16].

IR spectra were recorded on a Perkin–Elmer PE 883 IR spectrophotometer (4000–400 cm^{-1}) as nujol mulls between polyethylene pellets and KBr disks. ^1H- and $^{13}C\{^1H\}$-NMR spectra were recorded on Varian FT-300 and Varian FT-400 spectrometers and chemical shifts were measured relative to residual ^1H and ^{13}C resonances in the deuterated solvents. ^{13}C MAS-NMR spectra were recorded on Varian Infinity plus 400 Mz spectrometer. Elemental analyses were carried out with a Perkin–Elmer 2400 microanalyzer. Mass spectrometry analyses were performed on a Hewlett-Packard 5988 instrument.

4.2. Synthesis of [{Ti(OPr^i)$_3$(OAdam)}$_2$] (1)

Procedure A: a THF solution (40 ml) of adamantanol (0.4 g, 2.6 mmol) was added to a 1 M hexane solution of $TiCl(OPr^i)_3$ (2.6 ml, 2.60 mmol). After some minutes at room temperature (r.t.), NEt_3 (0.36 ml, 2.60 mmol) was added dropwise. The resulting suspension was stirred for 12 h and the solvent was then removed in vacuo. The crude reaction was extracted with hexane, $Et_3N{\cdot}HCl$ was filtered off, and washed two times with hexane. The solution was concentrated under reduced pressure and cooled at −30 °C, resulting a white solid (0.83 g, 84%). *Procedure B*: to a CH_2Cl_2 adamantanol solution (25 ml) (0.6 g, 3.90 mmol), $Ti(OPr^i)_4$ (1.18 ml, 3.90 mmol) was added. The solution was stirred at r.t. for 4 h, resulting a clear solution. The solvent and the free isopropyl alcohol produced were removed in vacuo. The crude white product can be recrystallized from hexane. Yield: 1.25 g, 85%. ^1H-NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.23 (d, 18H, $^3J_{H,H} = 6.04$ Hz, –CH(CH_3)$_2$), 1.57 (ps t, 6H, H_δ), 1.78 (ps d, 6H, H_β), 2.09 (m, 3H, H_γ), 4.47 (h, 3H, –C*H*(CH$_3$)$_2$); $^{13}C\{^1H\}$-NMR (300 MHz, $CDCl_3$, 25 °C): δ = 26.4 (–CH(*C*H$_3$)$_2$), 31.0 (C_δ), 36.2 (C_γ), 46.4 (C_β), 76.3 (–*C*H(CH$_3$)$_2$), 82.6 (C_α). IR (Nujol, cm^{-1}): 523(s), 615(br), 687(s), 756(s), 796(s), 812(m), 854(s), 999(s), 1115(s), 1329(s), 1349(s), 1361(s), 1376(s), 1451(m), 1464(m), 2623(w), 2655(w). $Ti_2C_{38}O_8H_{72}$—Calc.: C, 60.63; H, 9.64. Found: C, 60.27; H, 9.46%.

4.3. Synthesis of [{Ti(OPr^i)$_3$(ODAGP)}$_2$] (2)

Procedure A: the synthesis of **2** was carried out in an identical manner to **1**. 1,2:3,4-Di-*O*-isopropylidene-α-D-galactopyranose (0.5 g, 1.92 mmol), 1 M hexane solution of $TiCl(OPr^i)_3$ (1.92 ml, 1.92 mmol), and NEt_3 (0.30 ml, 1.92 mmol). Yield: 0.82 g, 88%, white solid. *Procedure B*: from 1,2:3,4-di-*O*-isopropilidene-α-D-galactopyranose (0.3 g, 1.1 mmol) and $Ti(OPr^i)_4$ (0.34 ml, 1.1 mmol). Yield: 0.48 g, 90%. ^1H-NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.22 (d, 18H, $^3J_{H,H} = 6.22$ Hz, –CH(CH_3)$_2$), 1.30 (s, 3H, CH_3), 1.32 (s, 3H, CH_3), 1.42 (s, 3H, CH_3), 1.52 (s, 3H, CH_3), 3.85 (m, 1H, C(5)–*H*), 4.26 (dd, 1H, $^3J_{H2,H3} = 2.12$ Hz, $^3J_{H2,H1} = 4.76$ Hz, C(2)–*H*), 4.38 (d, 1H, $^3J_{H4,H3} = 6.9$ Hz, C(4)–*H*), 4.4 (m, 2H, C(6)–*H*), 4.47 (h, 3H, –C*H*(CH$_3$)$_2$), 4.57 (dd, 1H, C(3)–*H*), 5.48 (d, 1H, $^3J_{H1,H2} = 4.76$ Hz, C(1)–*H*); $^{13}C\{^1H\}$-NMR (300 MHz, $CDCl_3$, 25 °C): δ = 24.4 (*C*H$_3$), 24.9 (*C*H$_3$), 26.0 (*C*H$_3$), 26.1 (*C*H$_3$), 26.5 (–CH(*C*H$_3$)$_2$), 68.3 (C_6), 70.4 (C_5), 70.6 (C_3), 70.8 (C_4), 72.9 (C_2), 77.2 (–*C*H(CH$_3$)$_2$), 96.3 (C_1), 108.3 (–*C*(CH$_3$)$_2$), 108.9 (–*C*(CH$_3$)$_2$). IR (KBr disk, cm^{-1}): 512(s), 634(br), 686(s), 770(m), 857(w), 900(w), 918(w), 1005(s), 1132(s), 1168(s), 1213(s), 1257(s), 1380(s), 2935(m), 2979(m). $Ti_2C_{42}O_{18}H_{80}$—Calc.: C, 52.07; H, 8.32. Found: C, 51.81; H, 8.20%.

4.4. Synthesis of [{Ti(OPr^i)$_3$(ODAGF)}$_2$] (3)

Procedure A: the synthesis of **3** was carried out in an identical manner to **1**. 1,2:5,6-Di-*O*-isopropylidene-α-D-glucofuranose (0.3 g, 1.10 mmol), 1 M hexane solution of $TiCl(OPr^i)_3$ (1.1 ml, 1.10 mmol), and NEt_3 (0.16 ml, 1.10 mmol). Yield: 0.43 g, 82%, colorless oil. *Procedure B*: from **1**. 1,2:5,6-Di-*O*-isopropilidene-α-D-glucofuranose (0.8 g, 3.1 mmol) and $Ti(OPr^i)_4$ (0.92 ml, 3.1 mmol). Yield: 1.2 g, 80%. ^1H-NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.21 (d, 18H, $^3J_{H,H} = 6.04$ Hz, –CH(CH_3)$_2$), 1.28 (s, 3H, CH_3), 1.32 (s, 3H, CH_3), 1.39 (s, 3H, CH_3), 1.45 (s, 3H, CH_3), 3.98 (m, 2H, C(6)–*H*), 4.08 (m, 1H, C(5)–*H*), 4.36 (m, 1H, C(4)–*H*), 4.47 (h, 3H, –C*H*(CH$_3$)$_2$), 4.53 (d, 1H, $^3J_{H2,H1} = 3.6$ Hz, C(2)–*H*), 4.75 (d, 1H, C(3)–*H*), 5.87 (d, 1H, C(1)–*H*); $^{13}C\{^1H\}$-NMR (300 MHz, $CDCl_3$, 25 °C): δ = 25.3 (*C*H$_3$), 26.3 (*C*H$_3$), 26.8 (*C*H$_3$), 26.4 (–CH(*C*H$_3$)$_2$), 67.2 (C_6), 72.5 (C_5), 77.2 (–*C*H(CH$_3$)$_2$), 82.5 (C_4), 85.05 (C_3), 86.03 (C_2), 105.2 (C_1), 108.9 (–*C*(CH$_3$)$_2$), 111.6 (–*C*(CH$_3$)$_2$). IR (Nujol-polyethylene, cm^{-1}): 629(br), 721(s), 733(s), 852(s), 908(s), 1015(m), 1075(m), 1126(m), 1165(s), 1216(s), 1302(s), 1377(m), 1459(s), 2945(s). $Ti_2C_{42}O_{18}H_{80}$—Calc.: C, 52.07; H, 8.32. Found: C, 51.50; H, 8.15%.

4.5. Synthesis of [{Ti(OPr^i)$_3$(OMent)}$_2$] (4)

Procedure A: the synthesis of **4** was carried out in an identical manner to **1**. 1*R*,2*S*,5*R*-(−)-Menthol (0.56 g, 3.50 mmol), 1 M hexane solution of $TiCl(OPr^i)_3$ (3.6 ml, 3.50 mmol), and NEt_3 (0.5 ml, 3.50 mmol). Yield: 1.15 g, 86%, colorless oil. *Procedure B*: from 1*R*,2*S*,5*R*-(−)-menthol (0.28 g, 1.78 mmol) and $Ti(OPr^i)_4$ (0.54 ml, 1.78 mmol). Yield: 0.58 g, 86%. ^1H-NMR (300 MHz, $CDCl_3$,

25 °C): $\delta = 0.75$ (d, 3H, $^3J_{H,H} = 6.9$ Hz, CH_3), 0.88 (d, 6H, $^3J_{H,H} = 6.6$ Hz, CH_3), 0.82–0.95 (m, 2H, C(4)–H), 1.09–1.16 (m, 2H, C(3)–H), 1.21 (d, 18H, $^3J_{H,H} = 6.04$ Hz, –CH(CH_3)$_2$), 1.26–1.4 (m, 1H, –CH), 1.5–1.61 (m, 2H, C(6)–H), 2.05 (m, 1H, C(2)–H), 2.34 (m, 1H, C(5)–H), 3.88 (m, 1H, C(1)–H), 4.45 (h, 3H, –CH(CH$_3$)$_2$); ^{13}C{^{1}H}-NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 15.8$ (*C*H$_3$), 21.1 (*C*H$_3$), 22.2 (*C*H$_3$), 22.7 (C$_3$), 25.5 (*C*H), 26.5 (–CH(*C*H$_3$)$_2$), 31.6 (C$_5$), 34.6 (C$_4$), 46.3 (C$_6$), 51.0 (C$_2$), 76.2 (–*C*H(CH$_3$)$_2$), 84.4 (C$_1$). IR (Nujol-polyethylene, cm^{-1}): 615(br), 725(s), 849(w), 1007(m), 1049(w), 1068(w), 1082(w), 1124(m), 1373(s), 1460(s), 2665(m). $TiC_{40}O_4H_{40}$—Calc.: C, 59.99; H, 10.60. Found: C, 59.10; H, 10.20%.

4.6. Synthesis of [{Ti(OPr^i)$_2$(OAdam)$_2$}$_2$] (5)

Procedure A: to a THF solution (40 ml) of adamantanol (0.8 g, 5.26 mmol) was added a 0.42 M toluene solution of $TiCl_2(OPr^i)_2$ (6.19 ml, 2.63 mmol). After some minutes at r.t., NEt_3 (0.73 ml, 5.26 mmol) was added dropwise. The resulting suspension was stirred for 12 h and the solvent was then removed in vacuo. The crude reaction was extracted with Et_2O, $Et_3N{\cdot}HCl$ was filtered off and washed two times with Et_2O. An Et_2O solution was concentrated under reduced pressure and cooled at −30 °C, resulting colorless crystalline needles not suitable for X-ray studies. *Procedure B*: to a CH_2Cl_2 solution (25 ml) of adamantanol (0.5 g, 3.28 mmol), $Ti(OPr^i)_4$ (0.49 ml, 1.64 mmol) was added. This solution was stirred at r.t. for 4 h. The solvent and the free isopropyl alcohol were removed under vacuo. Yield: 0.62 g, 81% (1.05 g, 85%) white solid. ^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 1.24$ (d, 12H, $^3J_{H,H} = 6.22$ Hz, –CH(CH_3)$_2$), 1.58 (pst, 12H, H_δ), 1.81 (psd, 12H, H_β), 2.11 (m, 6H, H_γ), 4.48 (h, 2H, –CH(CH$_3$)$_2$); ^{13}C{^{1}H}-NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 26.6$ (–CH(*C*H$_3$)$_2$), 31.1 (C$_\delta$), 36.3 (C$_\gamma$), 46.5 (C$_\beta$), 76.0 (–*C*H(CH$_3$)$_2$), 80.0 (C$_\alpha$). IR (KBr disk, cm^{-1}): 615(br), 689(m), 756(m), 796(m), 931(w), 956(m), 1003(s), 1086(s), 1115(s), 1300(w), 1349(m), 1453(w), 2849(s), 2905(s). $Ti_2C_{52}O_8H_{88}$—Calc.: C, 66.65; H, 9.47. Found: C, 66.25; H, 9.32%.

4.7. Synthesis of [{Ti(OPr^i)$_2$(ODAGP)$_2$}$_2$] (6)

Procedure A: to a THF solution of 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (25 ml) (0.82 g, 3.15 mmol) was added a 0.42 M toluene solution of $TiCl_2(OPr^i)_2$ (3.7 ml, 1.57 mmol). After some minutes at r.t., NEt_3 (0.44 ml, 3.15 mmol) was added dropwise. The resulting suspension was stirred for 12 h and the solvent was then removed in vacuo. The crude reaction was extracted with hexane, $Et_3N{\cdot}HCl$ was filtered off and washed two times with hexane. A white crystalline solid was obtained by concentrating and cooling (−30 °C) the solution (0.82 g, 88%). *Procedure B*: from 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (0.33 g, 1.30 mmol) and $Ti(OPr^i)_4$ (0.2 ml, 0.64 mmol). Yield: 0.37 g, 86%. ^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 1.25$ (d, 12H, $^3J_{H,H} = 6.04$ Hz, –CH(CH_3)$_2$), 1.32 (s, 6H, CH_3), 1.34 (s, 6H, CH_3), 1.43 (s, 6H, CH_3), 1.53 (s, 6H, CH_3), 3.89 (m, 2H, C(5)–H), 4.29 (dd, 2H, $^3J_{H2,H3} = 2.12$ Hz, $^3J_{H2,H1} = 4.76$ Hz, C(2)–H), 4.42 (d, 2H, $^3J_{H4,H3} = 6.9$ Hz, C(4)–H), 4.42 (m, 4H, C(6)–H), 4.51 (h, 2H, –CH(CH$_3$)$_2$), 4.60 (dd, 2H, C(3)–H), 5.51 (d, 2H, C(1)–H). ^{13}C{^{1}H}-NMR (300 MHz, $CDCl_3$, 25 °C): δ 24.4 (*C*H$_3$), 25.0 (*C*H$_3$), 26.0 (*C*H$_3$), 26.1 (*C*H$_3$), 26.5 (–CH(*C*H$_3$)$_2$), 68.3 (C$_6$), 70.5 (C$_5$), 70.6 (C$_3$), 70.8 (C$_4$), 73.3 (C$_2$), 77.0 (–*C*H(CH$_3$)$_2$), 96.3 (C$_1$), 108.3 (–*C*(CH$_3$)$_2$), 108.9 (–*C*(CH$_3$)$_2$). IR (KBr disk, cm^{-1}): 513(w), 631(br), 858(w), 889(w), 904(w), 1007(s), 1076(s), 1171(m), 1209(s), 1257(m), 1381(m), 1460(w), 2931(m), 2993(m). MS (FAB) *m*/*z*: 1368 [M$^+$, 5%], 1309 [M$^+$–CH(CH$_3$)$_2$, 7%]. $Ti_2C_{60}O_{28}H_{104}$—Calc.: C, 52.63; H, 7.66. Found: C, 52.32; H, 7.54%.

4.8. Synthesis of [{Ti(OPr^i)$_2$(ODAGF)$_2$}$_2$] (7)

Procedure A: to a THF solution of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (25 ml) (0.66 g, 2.50 mmol) was added a 0.42 M toluene solution of $TiCl_2(OPr^i)_2$ (1.8 ml, 1.25 mmol). After some minutes at r.t., NEt_3 (0.35 ml, 2.50 mmol) was added dropwise. The resulting suspension was stirred for 12 h and the solvent was then removed in vacuo. The crude reaction was extracted with Et_2O, $Et_3N{\cdot}HCl$ was filtered off and washed two times with Et_2O. The solution was concentrated under reduced pressure and cooled at −30 °C, resulting a white solid (0.67 g, 78%). *Procedure B*: from 1,2:5,6-di-*O*-isopropilidene-α-D-glucofuranose (0.8 g, 3.10 mmol) and $Ti(OPr^i)_4$ (0.46 ml, 1.55 mmol). Yield: 0.9 g, 85%. ^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.23 (d, 12H, $^3J_{H,H} = 6.04$ Hz, –CH(CH_3)$_2$), 1.28 (s, 6H, CH_3), 1.33 (s, 6H, CH_3), 1.40 (s, 6H, CH_3), 1.46 (s, 6H, CH_3), 3.99 (m, 4H, C(6)–H), 4.08 (m, 2H, C(5)–H), 4.34 (h, 2H, –CH(CH$_3$)$_2$), 4.45 (d, 2H, C(3)–H), 4.52 (d, 2H, $^3J_{H2,H1} = 3.5$ Hz, C(2)–H), 4.85 (m, 2H, C(4)–H), 5.86 (d, 2H, C(1)–H); ^{13}C{^{1}H}-NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 25.4$ (*C*H$_3$), 26.4 (*C*H$_3$), 26.9 (*C*H$_3$), 26.2 (–CH(*C*H$_3$)$_2$), 67.2 (C$_6$), 72.4 (C$_5$), 77.2 (–*C*H(CH$_3$)$_2$), 82.4 (C$_4$), 84.4 (C$_3$), 85.9 (C$_2$), 105.1 (C$_1$), 108.9 (–*C*(CH$_3$)$_2$), 111.6 (–*C*(CH$_3$)$_2$). IR (Nujol-polyethylene, cm^{-1}): 636(br), 725(s), 843(w), 951(w), 1014(m), 1072(m), 1165(m), 1219(m), 1255(m), 1302(m), 1377(s), 1462(s). $Ti_2C_{60}O_{28}H_{104}$—Calc.: C, 52.63; H, 7.66. Found: C, 52.42; H, 7.33%.

4.9. Synthesis of [{Ti(OPr^i)$_2$(OMent)$_2$}$_2$] (8)

Procedure A: to a THF solution of 1*R*,2*S*,5*R*-(−)-menthol (25 ml) (0.8 g, 5.1 mmol) was added a 0.69 M

toluene solution of $TiCl_2(OPr^i)_2$ (3.7 ml, 2.50 mmol). After some minutes at r.t., NEt_3 (0.71 ml, 5.10 mmol) was added dropwise. The resulting suspension was stirred for 12 h and the solvent was then removed in vacuo. The crude reaction was extracted with Et_2O, $Et_3N{\cdot}HCl$ was filtered off and washed two times with Et_2O. The resulting product was a colorless oil spectroscopically pure (0.98 g, 83%). *Procedure B*: from 1*R*,2*S*,5*R*-(−)-menthol (1.1 g, 7.03 mmol) and $Ti(OPr^i)_4$ (1.05 ml, 3.51 mmol). Yield: 1.51 g, 90%. ^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 0.77$ (d, 6H, $^3J_{H,H} = 6.09$ Hz, CH_3), 0.91 (d, 12H, $^3J_{H,H} = 6.6$ Hz, CH_3), 0.80–0.95 (m, 4H, C(4)–*H*), 1.04–1.15 (m, 4H, C(3)–*H*), 1.21 (d, 12H, $^3J_{H,H} = 6.22$ Hz, –CH(CH_3)$_2$), 1.3–1.45 (m, 2H, –C*H*), 1.52–1.64 (m, 4H, C(6)–*H*), 2.07 (m, 2H, C(2)–*H*), 2.36 (m, 2H, C(5)–*H*), 3.88 (m, 2H, C(1)–*H*), 4.48 (h, 2H, –C*H*(CH$_3$)$_2$); ^{13}C{^{1}H}-NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 15.8$ (*C*H$_3$), 21.1 (*C*H$_3$), 22.3 (*C*H$_3$), 22.7 (C$_3$), 25.5 (CH), 26.5 (–CH(*C*H$_3$)$_2$), 31.6 (C$_5$), 34.65 (C$_4$), 46.4 (C$_6$), 51.1 (C$_2$), 76.1 (–*C*H(CH$_3$)$_2$), 84.2 (C$_1$). IR (Nujol-polyethylene, cm^{-1}): 613(br), 725(s), 852(w), 997(m), 1049(m), 1064(m), 1080(m), 1105(m), 1373(s), 1460(s), 2661(m), 2729(m). MS (FAB) *m*/*z*: 953 [M$^+$, 23%], 879 [M$^+$–CH$_3$–CH(CH$_3$)$_2$, 100%]. $Ti_2C_{52}O_8H_{104}$—Calc.: C, 65.63; H, 11.00. Found: C, 65.10; H, 10.98%.

4.10. Synthesis of [Ti(OAdam)$_4$] (**9**)

To a CH_2Cl_2 adamantanol solution (25 ml) (1.4 g, 9.20 mmol) $Ti(OPr^i)_4$ (0.69 ml, 2.3 mmol) was added dropwise. The mixture was stirred for 6 h and the volatiles were removed getting a white solid (1.33 g, 89%). The crude product was recrystallized from CH_2Cl_2 to obtain a white crystalline solid. ^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 1.59$ (ps t, 24H, H_δ), 1.81 (ps d, 24H, H_β), 2.12 (m, 12H, H_γ); ^{13}C{^{1}H}-NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 31.1$ (C$_\delta$), 36.4 (C$_\gamma$), 46.6 (C$_\beta$), 79.1 (C$_\alpha$). IR (KBr disk, cm^{-1}): 689(s), 754(s), 796(s), 932(w), 955(s), 1001(s), 1084(s), 1113(s), 1299(m), 1311(w), 1348(s), 1452(m), 2846(s), 2902(m). $TiC_{40}H_{60}O_4$—Calc.: C, 73.60; H, 9.26. Found: C, 73.51; H, 9.91%.

4.11. Synthesis of [Ti(ODAGP)$_4$] (**10**)

To a CH_2Cl_2 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose solution (25 ml) (1.02 g, 3.90 mmol) $Ti(OPr^i)_4$ (0.29 ml, 0.97 mmol) was added dropwise. The mixture was stirred for 6 h and the volatiles were removed getting a white solid (0.95 g, 90%). A white crystalline solid was obtained by layering a saturated toluene solution with hexane (ratio 1:1) to r.t. ^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 1.32$ (s, 24H, CH_3), 1.43 (s, 12H, CH_3), 1.51 (s, 12H, CH_3), 2.36 (m, 4H, C(5)–*H*), 3.78 (m, 8H, C(6)–*H*), 4.25 (d, 4H, $^3J_{H4,H3} = 7.9$ Hz, C(4)–*H*), 4.32 (dd, 4H, $^3J_{H2,H3} = 1.55$ Hz, $^3J_{H2,H1} = 4.84$ Hz, C(2)–*H*), 4.58 (dd, 4H, C(3)–H), 5.55 (d, 4H, C(1)–*H*); ^{13}C{^{1}H}-NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 24.5$ (*C*H$_3$), 25.1 (*C*H$_3$), 26.1 (*C*H$_3$), 26.2 (*C*H$_3$), 67.3 (C$_6$), 72.3 (C$_5$), 82.2 (C$_3$), 85.6 (C$_4$), 86.6 (C$_2$), 104.9 (C$_1$), 109.1 (–*C*(CH$_3$)$_2$), 111.7 (–*C*(CH$_3$)$_2$). IR (KBr disk, cm^{-1}): 505(w), 646(br), 858(w), 889(w), 893(w), 999(s), 1068(s), 1171(m), 1209(s), 1257(m), 1381(m), 1460(w), 2939(m), 2985(m). $TiC_{48}H_{76}O_{24}$—Calc.: C, 53.14; H, 7.06. Found: C, 52.85; H, 7.01%.

4.12. Synthesis of [Ti(ODAGF)$_4$] (**11**)

To a CH_2Cl_2 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose solution (25 ml) (1.5 g, 5.70 mmol) $Ti(OPr^i)_4$ (0.43 ml, 1.4 mmol) was added dropwise. The mixture was stirred for 6 h and then the volatiles were removed in vacuo getting a white solid (1.3 g, 86%). The crude product was recrystallized from hexane to obtain a white crystalline solid. ^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 1.27$ (s, 12H, CH_3), 1.33 (s, 12H, CH_3), 1.39 (s, 12H, CH_3), 1.45 (s, 12H, CH_3), 3.98 (m, 8H, C(6)–*H*), 4.06 (dd, 4H, $^3J_{H4,H5} = 6.3$ Hz, $^3J_{H4,H3} = 2.34$ Hz, C(4)–*H*), 4.31 (m, 4H, C(5)–*H*), 4.52 (d, 4H, $^3J_{H2,H1} = 3.52$ Hz, C(2)–*H*), 4.96 (d, 4H, C(3)–*H*), 5.86 (d, 4H, C(1)–*H*); ^{13}C{^{1}H}-NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 25.4$ (*C*H$_3$), 26.3 (*C*H$_3$), 26.8 (*C*H$_3$), 27.0 (*C*H$_3$), 67.3 (C$_6$), 72.3 (C$_4$), 82.2 (C$_5$), 85.6 (C$_2$), 86.6 (C$_3$), 104.9 (C$_1$), 109.1 (–*C*(CH$_3$)$_2$), 111.7 (–*C*(CH$_3$)$_2$). IR (KBr disk, cm^{-1}): 634(br), 737(w), 812(w), 843(m), 883(w), 951(w), 1014(s), 1072(s), 1165(s), 1219(s), 1257(s), 1340(w), 1383(s), 1458(w), 2891(m), 2941(m), 2985(s). $TiC_{48}H_{76}O_{24}$—Calc.: C, 53.14; H, 7.06. Found: C, 53.06; H, 6.96%.

4.13. Synthesis of [Ti(OMent)$_4$] (**12**)

To a CH_2Cl_2 1*R*,2*S*,5*R*-(−)-menthol solution (25 ml) (1.9 g, 12.15 mmol) $Ti(OPr^i)_4$ (0.9 ml, 3.03 mmol) was added dropwise. The mixture was stirred for 6 h, then the volatiles were removed getting a colorless oil spectroscopically pure (1.76 g, 87%). ^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 0.78$ (d, 12H, $^3J_{H,H} = 6.9$ Hz, CH_3), 0.9 (d, 24H, $^3J_{H,H} = 6.4$ Hz, CH_3), 0.81–0.93 (m, 8H, C(4)–*H*), 1.10–1.21 (m, 8H, C(3)–*H*), 1.29–1.4 (m, 4H, –C*H*), 1.5–1.63 (m, 8H, C(6)–*H*), 2.09 (m, 4H, C(2)–*H*), 2.35 (m, 4H, C(5)–*H*), 3.87 (m, 4H, C(1)–*H*); ^{13}C{^{1}H}-NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 15.8$ (*C*H$_3$), 21.2 (*C*H$_3$), 22.3 (*C*H$_3$), 22.7 (C$_3$), 25.5 (CH), 31.7 (C$_5$), 34.6 (C$_4$), 46.5 (C$_6$), 51.0 (C$_2$), 84.1 (C$_1$). IR (Nujol-polyethylene, cm^{-1}): 725(s), 849(w), 928(w), 1045(m), 1049(m), 1065(m), 1080(m), 1105(m), 1304(w), 1373(s), 1460(s), 2360(w), 2665(m). $TiC_{40}H_{76}O_4$—Calc.: C, 71.82; H, 11.45. Found: C, 71.06; H, 11.32%.

4.14. General procedure for the catalytic asymmetric epoxidation (epoxycinnamyl alcohol)

Entry 1: a flame-dried 250 ml two-necked flask was fitted with dropping funnel and flushed with nitrogen, and charged with 2 g of activated, powdered 4 Å molecular sieves, 0.54 g (0.79 mmol) of **6** and 100 ml of dry CH_2Cl_2. After the mixture was cooled to -20 °C 5.7 ml of a 5.5 M solution of TBHP in nonane (31.4 mmol) was added. The mixture was stirred at -20 °C for 1 h and then treated with 3.2 ml of a 4.8 M solution of freshly distilled (*E*)-3-phenyl-2-propenol (cinnamyl alcohol) in CH_2Cl_2 (15.7 mmol), added dropwise over 1 h. The resulting homogeneous solution was stored for 5 h at -20 °C. After the reaction mixture is quenched with 0.4 ml of a 10% aqueous solution of sodium hydroxide it is saturated with sodium chloride. After the cold bath is removed and stirred mixture is maintained for 10 min. Then the mixture was treated with $MgSO_4$ and Celite, and after that the solution is filtered, washing with Et_2O. The volatiles were removed in vacuo getting a yellow oil (1.6 g, yield: 65%, 22% ee determined by HPLC with a chiralpack AD-H 250 × 4.6 μm column from VWR International Eurolab). ^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 2.15$ (br s, 1H, –OH), 3.22–3.25 (m, 1H, –CH), 3.81 (dd, 1H, $-CH_2$), 3.94 (d, 1H, –CH), 4.06 (dd, 1H, $-CH_2$), 7.2–7.4 (m, 5H, C_6H_5). *Entry 2*: epoxidation of cinnamyl alcohol using catalyst **7** was carried out as described for **6**. 100 ml CH_2Cl_2 with 2 g of activated, powdered 4 Å molecular sieves, 0.53 g (0.7 mmol) of **7**, 5.4 ml of a 5.5 M solution of TBHP in nonane (30 mmol), and 3 ml of a 4.8 M solution of freshly distilled (*E*)-3-phenyl-2-propenol (cinnamyl alcohol) in CH_2Cl_2 (15 mmol) (1.28 g, yield: 60%, 17% ee determined by HPLC with a chiralpack AD-H 250 × 4.6 μm column from VWR International Eurolab).

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