Titanium complexes based on chiral enantiopure dialkanolamines: synthesis, structures and catalytic activity†

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New chiral enantiopure tridentate ligands (dialkanolamines) $RN(CHR^3CR^1R^2OH)(CHR^4CR^5R^6OH)$ **10–17** were synthesized by the opening of the epoxide ring by the action of the amines or alkanolamines. Titanium complexes, *viz*. $[RN(CHR^3CR^1R^2O)(CHR^4CR^5R^6O)]Ti(O\text{-}i\text{-}Pr)_2$ **18–23** and $[RN(CHR^3CR^1R^2O)(CHR^4CR^5R^6O)]_2Ti$ **25–31** were synthesized by treatment of $Ti(O\text{-}i\text{-}Pr)_4$ with one or two equivalents of corresponding dialkanolamines. Complex (*R*)-$PhCH(Me)N(CH_2C(Me)_2O)_2TiCl_2$*$HNMe_2$ **24** was obtained from the reaction of one equivalent of dialkanolamine **10** with $(Me_2N)_2TiCl_2$. The composition and structure of all novel compounds were established by ^1H and ^{13}C NMR spectroscopy as well as elemental analysis. The possible solution structures of **18–31** are discussed. The single-crystal X-ray diffraction study of **23**, **25–28**, **30**, **31** indicates monomeric structures in the solid state. Chiral complexes **20**, **22**, **23**, **25**, **26**, **30** were tested as chiral catalysts in the Abramov reaction and demonstrated moderate enantiomeric activity.

Introduction

The complexes of titanium are very important for modern chemistry and catalysis.[1] One of the current trends in the chemistry is the use of polydentate ligands for synthesis of metal complexes which may be applied as catalysts for fine organic reactions or processes of polymerization. Within this field, ligands featuring anionic oxygen donors (alkoxides, aryloxides)[2] and especially alkoxides with an additional intramolecular donor group attract the attention of scientists.[3–7] This group may form a transannular bond with the titanium atom. The presence of such a bond in molecules allows control of the structural and electronic parameters of the Ti derivatives such as the coordination number of titanium atom as well as its coordination polyhedron and Lewis acidity and hence variation in the catalytic properties. Among these compounds the derivatives of trialkanolamines (titanatranes) have been investigated extensively.[3] The derivatives of dialkanolamines (titanocanes and spirobititanocanes) are much less studied.[4] However, these classes of compounds are more attractive for investigation due to their greater chemical and structural flexibility.

The preparation of the chiral ligands which possess the ability for effective transfer of chirality to metal is a crucial factor for successful asymmetric metal catalysis. Thus, the construction of the new ligands is a real problem for modern chemistry. Titanium complexes with chiral dialkanolamines have also been used in several catalytic applications such as epoxidation of allylic alcohols,[4a] Diels–Alder and ene-reactions[4c] and polymerization.[4b,d–f] However, the actual structure of the titanium complexes involved in catalysis in some of these reactions[4c–e] still needs to be clarified.

In continuation of our studies on Ti(IV) complexes[8] we present the synthesis and characterization of the new chiral dialkanolamines and cyclic Ti alkoxides with transannular interaction.

Results and discussion

Ligand precursors

The ligand precursors **9–17** have been synthesized *via* the nucleophilic ring opening of epoxides **4–6** by the different enantiopure amines or alkanolamines **1–3** (Scheme 1). Forcing conditions (excess of epoxide, high temperature) are required to drive the reaction to completion.

The reaction of **9** with 2,2-diphenyloxirane **5** did not give the desired product even at elevated temperatures. Synthesis of **9–13** and **16**, **17** proceeded regiospecifically. In the reaction of **2** with **6** there is formed the inseparable mixture of two possible regioisomers **14** and **15** with prevalence of expected compound **14** (**14** : **15** = 9 : 1 according to ^1H NMR spectroscopy data).[9] So the direction of the epoxide opening

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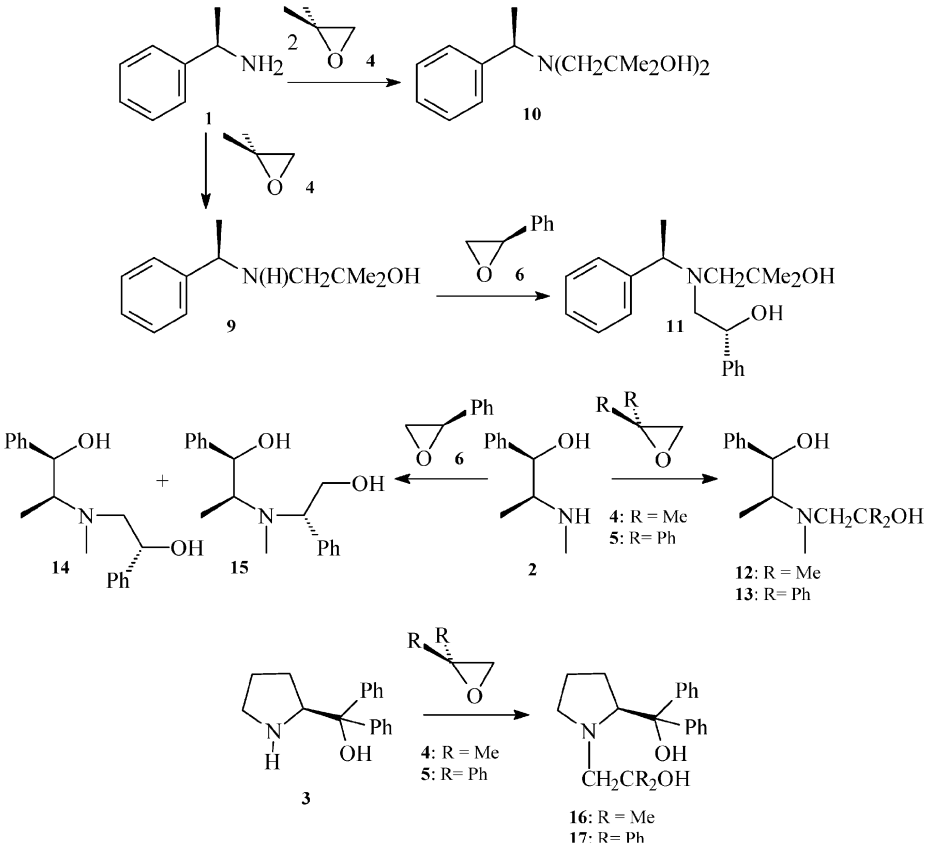


Scheme 1 Synthesis of dialkanolamines **9–17**.

reaction depends on the steric requirements of the reagents and on the nature of epoxide.

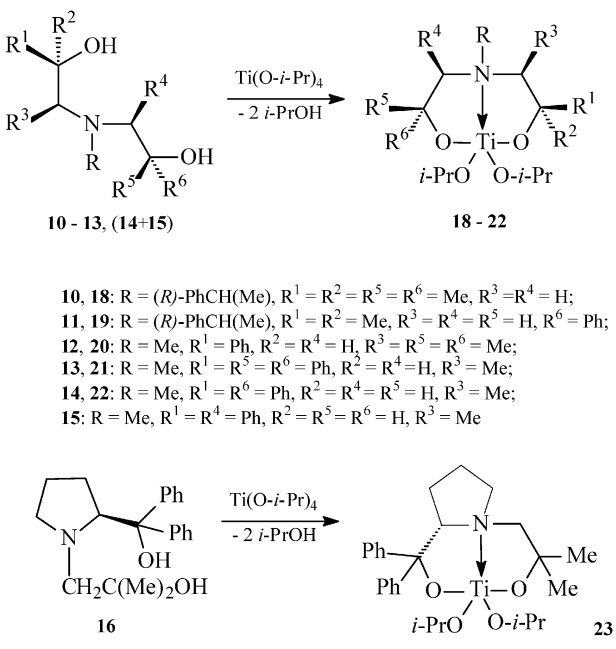
The reactions proceeded enantiospecifically. The enantiomeric purity of synthesized dialkanolamines was confirmed by ^{1}H NMR spectroscopy data using chiral solvating agents[10,11] such as (1*S*)-(+)-camphor-10-sulfonic acid monohydrate **7**[12] or *O*-acetyl-(*S*)-(+)-mandelic acid **8**.[13]

All compounds were characterized by ^{1}H and ^{13}C NMR spectroscopy, elemental analysis and in several cases by mass spectrometry. The presence of hydrogen bonds leads to appearance of diastereotopic CH_2, $C(CH_3)_2$ and CPh_2 groups in NMR spectra.[14]

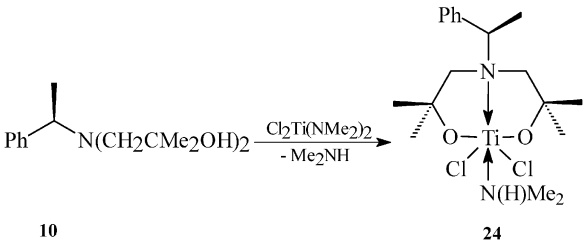
Titanocanes

Two types of titanocanes—dialkoxytitanocanes **18–22** and dichlorotitanocane **24**—were obtained in this work. Compounds were characterized by ^{1}H and ^{13}C NMR spectroscopy and by elemental analysis. The prepared complexes are air- and moisture sensitive, and in several cases this complicates the obtaining of satisfactory results of the elemental analysis. According to the literature, the most suitable approach to the dialkoxy derivatives of Ti with chelate ligands is the transalkoxylation of $Ti(OAlk)_4$ with the free ligand precursor containing two OH groups.[2–5,6*d*,*e*,*j*,*n*,*p*,7,8] We have found that dialkanolamines **10–13**, (**14** + **15**), **16** reacted readily with the equimolar amount of $Ti(O\text{-}i\text{-}Pr)_4$ in chloroform or toluene solution to give the corresponding titanocanes **18–23** in high yields (Scheme 2). The inseparable mixture of **14** and **15** gave only one product, **22**, after crystallization.

Compound **24** was obtained by alkoxydesamination reaction of $Cl_2Ti(NMe_2)_2$ with dialkanolamine **10** (Scheme 3). In this complex the steric volume of chlorine atoms allows the intermolecular coordination of an $N(H)Me_2$ molecule formed in the course of the reaction.



Scheme 2 Synthesis of titanocanes **18–23**.



10 24

Scheme 3 Synthesis of titanocane **24**.

One of the most important questions in the chemistry of titanium is the coordination state of the Ti atom in the solid state and in solution. In general, titanium complexes exhibit a monomeric structure with a pentacoordinate (trigonal bipyramidal) coordination environment and also a dimeric structure with a hexacoordinate titanium atoms (octahedral geometry).[15] According to the literature, most of diisopropoxytitanocanes are monomeric in the solid state and in solution.[4f,8b] Moreover, the presence of steric groups such as CMe_2, Ph, CPh_2 in the titanocane 'ocane' skeleton leads to preferential formation of monomeric complexes. The four possible geometric isomers for a pentagonal Ti atom with overall molecular symmetry are presented in the Scheme 4. The structures are distinguished by the disposition of the ligand frameworks (*mer*-, *fac*-) and X groups (*cis*-, *trans*-). The structure **D** is less possible due to geometric reasons and the structure **C** is typical only for pyridine or imine derivatives.[7,8c] In the structures **A**, **B** the titanium atom is chiral (in case **B**, when a substituent is bound to a carbon atom of the ocane skeleton).

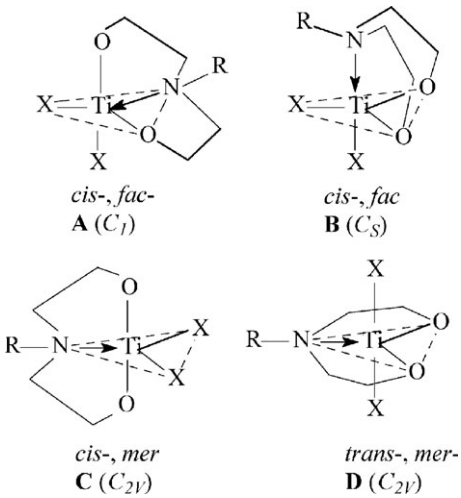
The solid-state structure of **23** was determined by single-crystal X-ray diffraction study (Table 1, Fig. 1). Prior to this work, only one diisopropoxytitanocane has been structurally characterized by X-ray analysis.[4f] Compound **23** is monomeric and Ti atom has the structure of type **B** in which nitrogen atom and one of the *i*-PrO groups occupy the axial positions. The Ti–O bond distances (1.789(2) Å for Ti–O_{ax} and 1.823(2)–1.869(2) Å for Ti–O_{eq}) are close to those previously found for $PhCH_2N(CH_2C(Me)_2O)_2Ti(O\text{-}i\text{-}Pr)_2$ (1.786(1) Å and 1.810(1)–1.852(1) Å, respectively).[4f] Somewhat shorter Ti–N bond distance (2.316(2) Å in **23** and 2.447(1) Å in $PhCH_2N(CH_2C(Me)_2O)_2Ti(O\text{-}i\text{-}Pr)_2$) is caused possibly by the structural and electronic properties of ligand **16**. So in titanocanes the modification of the structure of dialkanolamines leads to a noticeable change only in the Ti–N bond distance. The five-membered rings of the ocane skeleton adopt a twist-like ($TiOC(Ph)_2CHN$) or an envelope-like ($TiOC(Me)_2CH_2N$) conformation. The pyrrolidine ring has a twist conformation. The crystal of compound **23** is chiral (the space group is $P2_12_12_1$, $Z = 4$). Due to the presence of transannular Ti–N bond, the nitrogen atom is stereogenic and has an (*R*)-configuration.

Table 1 Selected bond distances (Å) and angles (°) for **23**

Ti(1)–O(4)	1.789(2)	C(5)–O(4)–Ti(1)	164.4(2)
Ti(1)–O(3)	1.823(2)	O(3)–Ti(1)–O(1)	114.9(1)
Ti(1)–O(1)	1.837(2)	O(3)–Ti(1)–O(2)	114.40(9)
Ti(1)–O(2)	1.869(2)	O(1)–Ti(1)–O(2)	122.62(9)
Ti(1)–N(1)	2.316(2)	O(4)–Ti(1)–N(1)	169.50(9)
C(1)–O(1)–Ti(1)	128.4(2)	O(3)–Ti(1)–N(1)	87.19(9)
C(11)–O(2)–Ti(1)	127.9(2)	O(1)–Ti(1)–N(1)	76.72(9)
C(8)–O(3)–Ti(1)	131.7(2)	O(2)–Ti(1)–N(1)	76.47(8)

In solution all compounds are expected to show coordination of the N atom to the Ti as a result of the electron deficiency on the metal centre. The circumstantial evidence of this bonding is a shift of signals of NCH_3, NCH_2 or NCH groups in the ^1H and ^{13}C NMR spectra to lower field in comparison with the corresponding non-coordinated ligands.

The ^1H NMR spectrum of **18** contains signals of diastereotopic NC*H*H and $OC(CH_3)_2$ groups. At the same time in ^{13}C NMR spectrum these groups are characterized by one set of signals. These data are consistent with an overall C_S-symmetry (structure of the type **B**). On this basis one may conclude that titanocanes **19–23** have the same structure in solution. Of interest, the NC*H*H and $OC(CH_3)_2$ proton resonances are somewhat broad and these data establish that **18**



Scheme 4 Schematic representations of the possible trigonal-bipyramidal coordination environments of a Ti atom in disubstituted titanocanes.

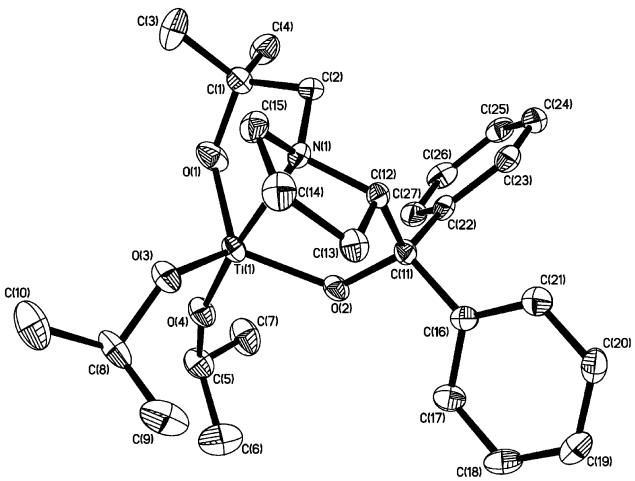
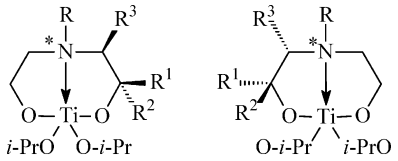


Fig. 1 Molecular structure of **23**. Displacement ellipsoids are drawn at the 50% probability level. All hydrogen atoms have been omitted for clarity.



Scheme 5 Schematic representations of two diastereomers of titanocanes.

undergoes exchange processes in the $NCH_2C(Me)_2O$ groups (Berry pseudorotation)[4f] and change in conformation of the five-membered chelate rings.

Complexes **19–23** are formed by dialkanolamines **11–13**, (**14** + **15**), **16** in which nitrogen atom has three different substituents. So in the corresponding titanocanes nitrogen atoms are optically active and these complexes may exist as two diastereomers **Ia** or **Ib** (Scheme 5).

The NMR spectra of titanocanes **20–22** contain in each case two sets of signals indicating that these compounds represent a mixture of two diastereomers (**Ia** or **Ib**) sometimes with preference for one of them. The ratio between these isomers varies in the range 1 : 1 to 11 : 1 and does not change with time. However titanocanes **19**, **23** were obtained as a single diastereomer.

In the ^{1}H NMR spectrum of **20**, raising the temperature ($C_6D_5CD_3$, 100 °C) results in broadening and coalescence of signals of two diastereomers **Ia** and **Ib**. These data establish that at elevated temperatures **20** undergoes Ti–N bond dissociation and exchange processes such as Berry pseudorotation and change in the chelate ring conformations.[4f,16] In contrast, raising the temperature in the case of **21** leads only to broadening of the signals in ^{1}H NMR spectrum indicating the dependence of solution behaviour of the titanocanes upon the structure of ligand.

In compound **24** the titanium atom is hexacoordinated. For this case four possible isomers distinguished by orientation of ligand framework (*mer*-, *fac*-), the chlorine (*cis*-, *trans*-) and nitrogen atoms (*cis*-, *trans*-) are presented in Scheme 6. It is evident that for Ti derivatives with dialkanolamines the *fac*-disposition of ligand is most suitable.

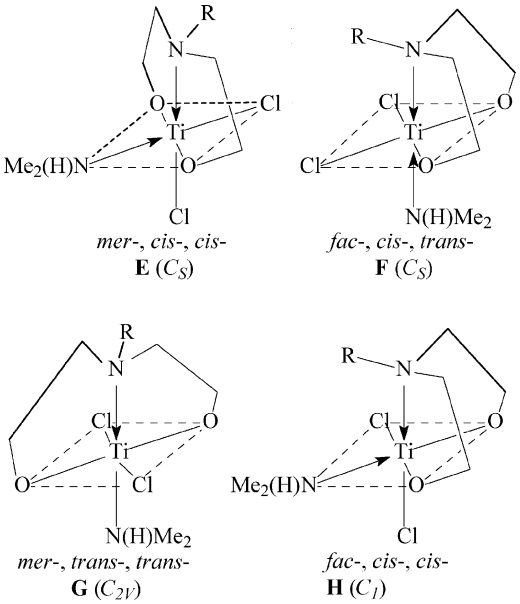
Key resonances include two AB doublets of the NC*H*H groups and two singlets of the $OC(CH_3)_2$ groups. The ^{13}C NMR spectrum of **24** contains one NCH_2 and one $OC(CH_3)_2$ resonances. These data are consistent with overall C_s-symmetry (structure **F**).

Spirobititanocanes

The transalkoxylation reaction of Ti(O-*i*-Pr)$_4$ with two equivalents of different dialkanolamines is the most suitable method for synthesis of spirobititanocanes.[4f,17] Compounds **25–31** were obtained using ligand precursors **10–13**, (**14** + **15**), **16**, **17** in toluene at reflux in high yields (Scheme 7).

In the case of inseparable mixture of dialkanolamines **14**, **15** the single product **29** was obtained after crystallization.

All complexes were investigated by ^{1}H and ^{13}C NMR spectroscopy, elemental analysis and in several cases by mass spectrometry.

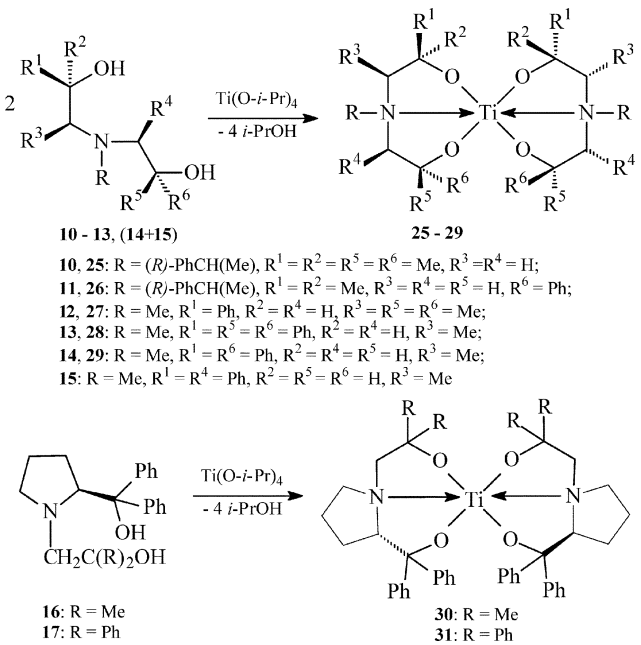


Scheme 6 Schematic representations of the octahedral coordination environment of Ti atom in **24**.

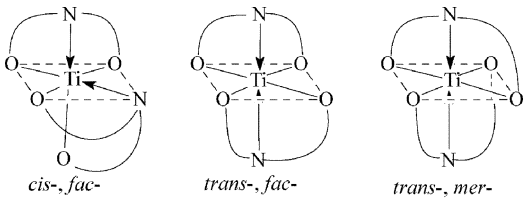
Previously eight spirobititanocanes have been investigated in the solid state by X-ray analysis.[8b,17] These compounds are monomeric due to existence of two transannular Ti–N bonds and the titanium atom shows octahedral coordination. The three possible geometric isomers for this case are given in Scheme 8.

The titanium atom in structure **I** has a chiral coordination environment. In the case of the unsymmetrically substituted at N atom ligands **11–17** the structures **J** and **K** are also chiral.

The structures of six spirobititanocanes **25–28**, **30** and **31** obtained in this work were determined by single-crystal X-ray analysis (Table 2, Fig. 2–7). All compounds are monomeric in the solid state. In **24–28**, **30** the titanium atoms are



Scheme 7 Synthesis of spirobititanocanes **25–31**.



Scheme 8 Schematic representations of the octahedral coordination environment of the Ti atom in the spirobititanocanes.

hexacoordinated with distorted octahedral coordination environment of central atom. In **31** the Ti polyhedron is characterized as a distorted trigonal prism, the planes of which are formed by the N atom, the O atom of the $OCPh_2$ group of the pyrrolidine ring and the O atom of the $OC(Ph)_2$ group from the other ligand framework. These planes are almost parallel (dihedral angle 1.18(7)°). To the best of our knowledge, compound **31** is the first example of such a structural type for titanium derivatives. Compounds **25–27**, **30** exhibit a *cis* disposition of the two N atoms (type **I**). On the contrary, the N atoms in **28** occupy the *trans*, *mer* positions of an octahedron (type **K**) in which the angle between the planes of O(21)–Ti–O(22) and O(11)–Ti–O(12) is equal to 89.7(1)°. Of interest, the pairs of related compounds which differ only in substituents in OCR^1R^2 groups (**27** and **28**, **30** and **31**) have different geometric structures. Introduction of the more bulky groups in the ocane skeleton leads to maximum spatial divergence of the $OCR^1R^2CR^3R^4N$ groups that results in the structure of type **K** or very unusual for Ti trigonal prism instead of structural type **I** which is characteristic for unsubstituted spirobititanocanes.[8b,17] Thus one can conclude that the steric size of the ligand is the main factor governing the coordination environment around the metal centre in spirobititanocanes.

The Ti–N bond distances in **25–28**, **30** and **31** vary in the wide range (2.231(3)–2.842(3) Å). The shortest Ti–N distance (2.231(3) Å) is found in **28** with *trans* disposition of the N atoms. The largest Ti–N bond (2.842(3) Å) is found for **25** in

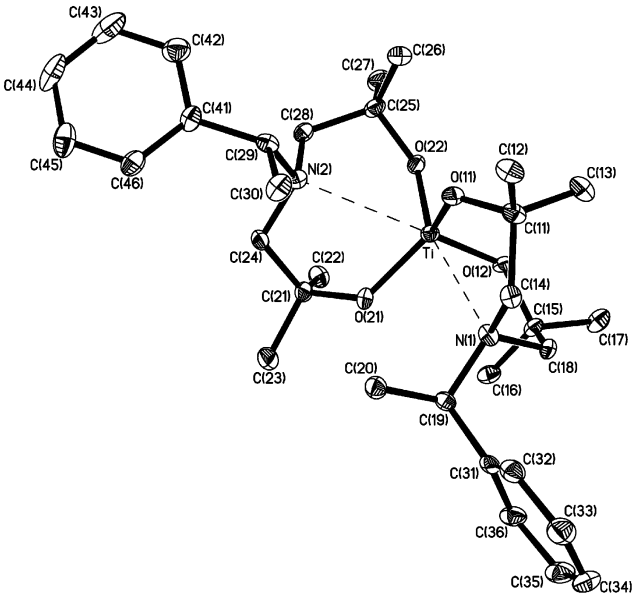


Fig. 2 Molecular structure of **25**. Displacement ellipsoids are drawn at the 50% probability level. All hydrogen atoms have been omitted for clarity.

which the N atoms carry (*R*)-PhCH(Me) substituents. Thus, Ti–N bond distances in spirobititanocanes depend on the steric volume of the substituent at the N atom, but not on its electronic properties. Of interest, the change of the organic group in the ocane skeleton of **25**, **26** results only in a significant change in the Ti–N bond distance. The Ti–O bond distances vary over the range (1.811(2)–2.910(2) Å) and depend on the nature of substituent in OCR^1R^2 groups. The shorter Ti–N bond in the molecule corresponds to the longer Ti–O bond.

Nitrogen atoms in **25–28**, **30** and **31** are chiral and have (*R*)-configuration. Crystals of these spirobititanocanes are chiral, too. The five-membered chelate rings adopt an envelope-like or twist conformation. The pyrrolidine ring in **30** and **31** adopts an envelope-like conformation.

Table 2 Selected bond distances (Å) and angles (°) for **25–28**, **30** and **31**

Compound	25	26	27	28	30	31
Ti–N	2.683(3)	2.598(2)	2.491(2)	2.231(3)	2.389(2)	2.355(2)
	2.842(3)	2.598(2)	2.543(2)	2.237(3)	2.485(2)	2.382(2)
$Ti–O_{trans\ to\ O}$	1.838(2)	1.856(2)	1.858(2)	1.874(2)	1.839(2)	1.862(2)
	1.844(2)	1.856(2)	1.878(2)	1.890(2)	1.844(2)	1.864(2)
				1.891(2)		1.878(2)
				1.910(2)		1.907(2)
$Ti–O_{trans\ to\ N}$	1.811(2)	1.828(2)	1.827(2)	—	1.871(2)	—
	1.819(2)	1.828(2)	1.840(2)		1.876(2)	
N–Ti–N	126.11(8)	116.46(8)	121.70(7)	159.7(1)	133.90(7)	146.46(7)
N(1)–Ti–O	71.09(9)	72.10(6)	73.82(7)	74.2(1)	73.25(7)	73.15(7)
	72.23(9)	74.20(6)	74.57(8)	74.9(1)	74.49(7)	73.47(7)
	81.11(9)	83.05(7)	82.53(8)	86.8(1)	85.98(7)	86.65(7)
	164.45(9)	166.13(6)	164.67(8)	122.1(1)	150.83(7)	137.80(7)
O–Ti–O	95.51(9)	96.9(1)	91.08(9)	91.8(1)	84.69(7)	83.00(7)
	106.2(1)	101.84(7)	106.85(8)	92.05(9)	102.12(8)	98.78(7)
	106.45(9)	101.85(7)	107.04(8)	95.6(1)	102.89(7)	99.45(7)
	111.9(1)	109.53(7)	107.29(8)	97.4(1)	118.06(7)	113.28(7)
	112.2(1)	109.53(7)	109.87(8)	145.68(9)	120.89(7)	131.49(7)
	121.6(1)	132.0(1)	128.34(8)	151.1(1)	122.74(8)	131.91(7)

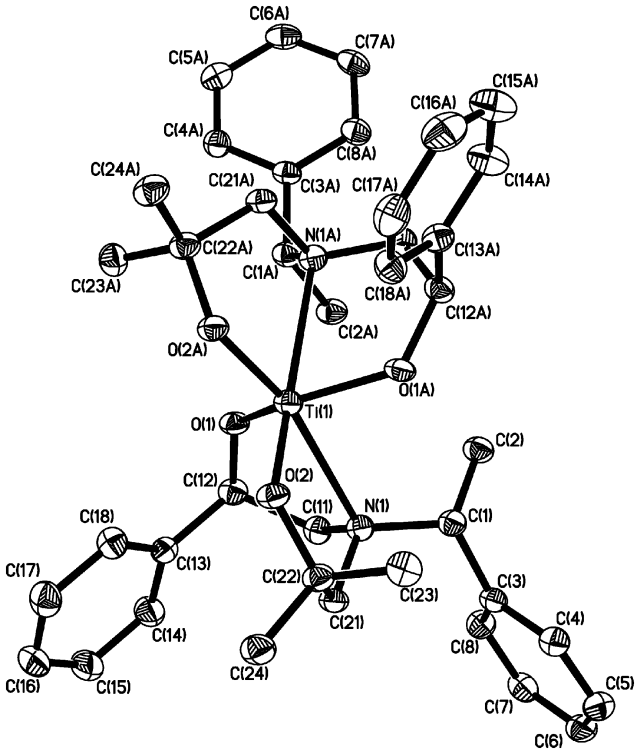


Fig. 3 Molecular structure of **26**. The molecule lies on crystallographic twofold axis and the additional "A" letter in the atom labels indicates that these atoms are at equivalent positions ($1 - x$, y, $0.5 - z$). Displacement ellipsoids are drawn at the 50% probability level. All hydrogen atoms have been omitted for clarity.

The signals of the CH_3, CH_2 and CH groups in the ^1H and ^{13}C NMR spectra of **25–31** are characterized by a low field shift ($\Delta\delta$ = 0.3–7.0 ppm) in comparison with those for free ligand precursors **10–13**, (**14** + **15**), **16**, **17** which could indicate Ti–N bonding in solution. This evidence and the data of X-ray analysis, mass spectrometry for **25**, **28**, **30** and the literature support monomeric structure of these spirobititanocanes in solution.[4f,8b,17]

In the ^1H NMR spectra of **25–31** the signals of C*H*(H)O or C*R*(R)O groups are diastereotopic. According to NMR spectral data, complex **25**, which was prepared from dialkanolamine **10** with two equal "arms" at N atom, is formed as a single isomer. The ^{13}C NMR spectrum of this derivative contains one set of signals for the $OC(Me)_2CH_2N$ group. These data are consistent with overall C_{2h} or S_2 symmetry (structural type **J** or **K**). The broadening of resonances in the ^1H NMR spectrum establishes the existence in solution of dynamic processes such as fast dissociation–formation of Ti–N bond and changing in chelate rings conformations.[16]

Spirobititanocanes **26–31** are obtained from the chiral unsymmetrically substituted dialkanolamines **11–13**, (**14** + **15**), **16**, **17**. So the three possible geometric isomers may form ten *fac* and/or two *mer* diastereomers. For the spirobititanocanes each geometric isomer may exist in form of three diastereomers differing in their N atom configuration (*S*,*S*; *R*,*R*; *S*,*R*/*R*,*S*). According to the X-ray analysis data the formation of derivatives with different configurations (*S*,*R*/*R*,*S*) is less favored. In the course of this work, we found that compounds **30**, **31** are obtained as a single

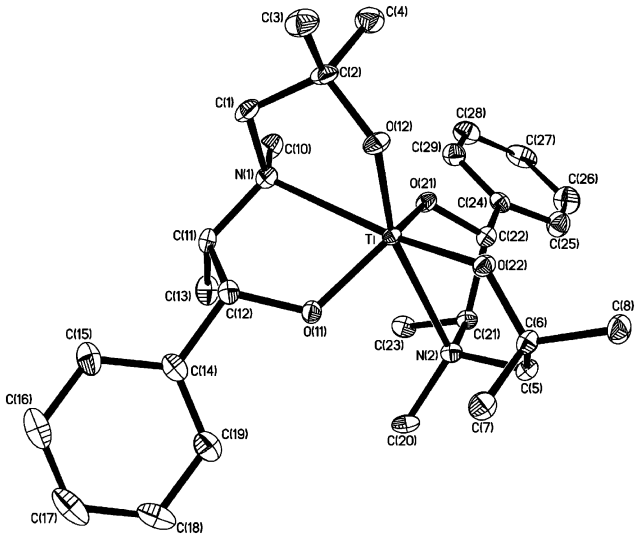


Fig. 4 Molecular structure of **27**. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms and dichloromethane molecule of crystallization have been omitted for clarity.

diastereomer. The NMR spectra of these derivatives contain one set of signals indicating C_2 symmetry for the molecule. The ^1H and ^{13}C NMR spectra of **27–29** contain two sets of signals which correspond to the existence of two diastereomers and according to ^1H NMR data, the ratio between them is equal to 4 : 1. The major isomer in **27–29** is characterized by one series of signals which are consistent with C_2 symmetry of the complex. The minor isomer in **27**, **29** conforms also to C_2 symmetry. On the

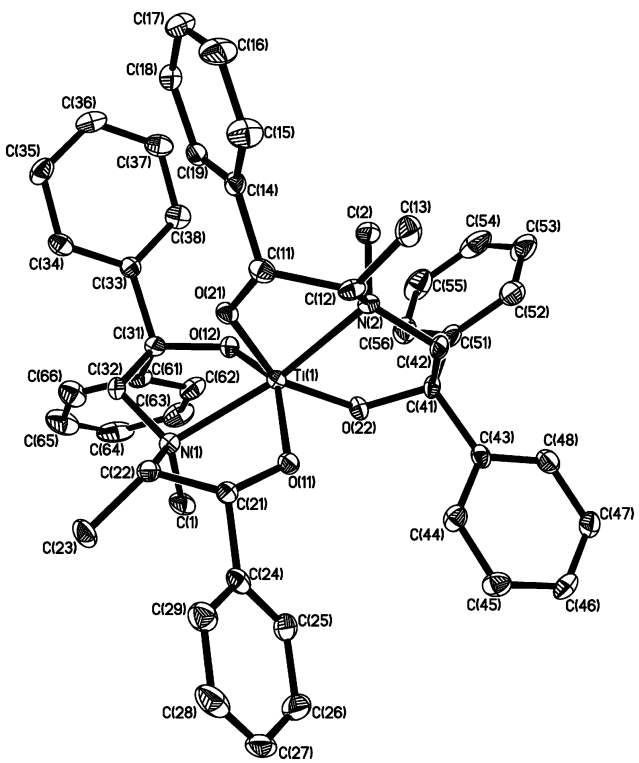


Fig. 5 Molecular structure of **28**. Displacement ellipsoids are drawn at the 50% probability level. All hydrogen atoms have been omitted for clarity.

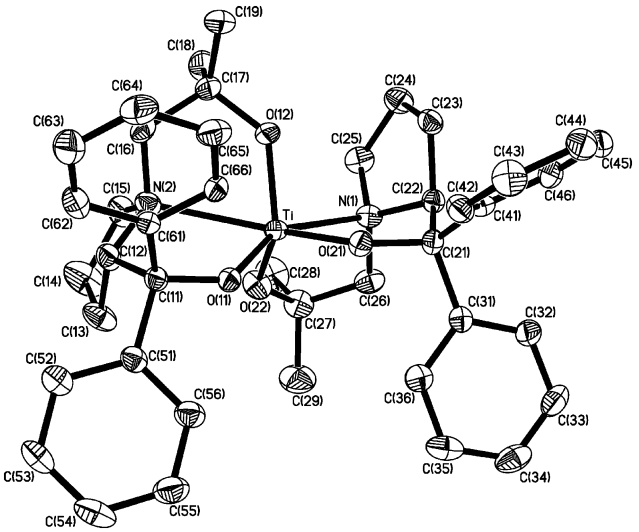


Fig. 6 Molecular structure of **30**. Displacement ellipsoids are drawn at the 50% probability level. All hydrogen atoms have been omitted for clarity.

contrary, the minor isomer in **28** may be characterized as a C_1 symmetry complex. The NMR spectra of **26** contain two sets of signals corresponding to inequivalent dialkanolamine frameworks within coordination sphere of the Ti atom, that is consistent with an overall C_1 molecular symmetry.

Catalytic activity

In the course of the Abramov reaction the dialkyl phosphite reacts with carbonyl compounds to give dialkyl α-hydroxy phosphonates. Chiral α-hydroxy phosphonates are biologically active and are flexible precursors for other α- and γ-substituted phosphonates.[18] The most efficient and economic route to these compounds involves enantioselective catalysis. In literature there are several reports in which the Ti alkoxides are used as Abramov reaction catalysts.[19] The ee values of the products vary over the range 7–70% depending on the nature of solvent, carbonyl compound and ligands used. We supposed that the derivatives of chiral dialkanolamines thus obtained may serve as enantioselective catalysts in phospho-aldol addition. It was important to study the catalytic activity of the titanium complexes in phosphonylation of carbonyl compounds and the dependence of the ee of the products on the structure of catalyst used.

The possible mechanism of the Abramov reaction in the case of titanocanes and spirobititanocanes is supposed to be similar to that proposed earlier[19a] and involves three basic stages including the coordination of carbonyl compound to Ti atom to form a hexacoordinated complex (in the case of spirobititanocanes with preliminary Ti–N bond dissociation), attack of the *meta* form of dialkyl phosphite, $P(OH)(OR)_2$, to a carbonyl group, regrouping of the adduct to form the reaction product and the catalyst and the dissociation of the intermediate. The ^{31}P NMR spectra of **25** in a mixture with diethyl and dimethyl phosphites are identical to the spectra of pure $HP(O)(OEt)_2$ and $HP(O)(OMe)_2$ so the alternative mechanism including the initial coordination of the *meta* form of dialkyl phosphite to the Ti centre is less possible.

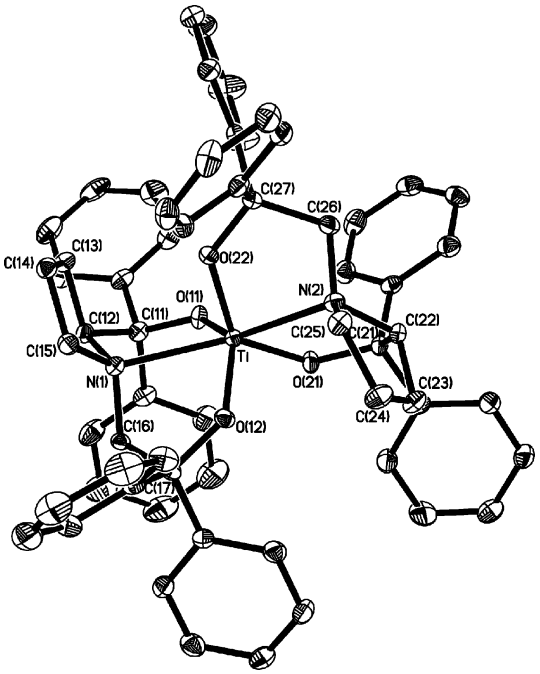


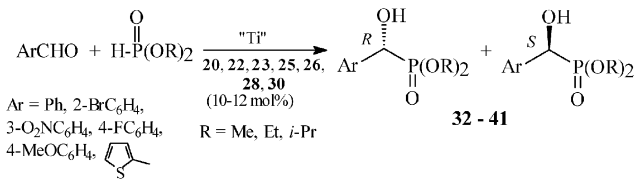
Fig. 7 Molecular structure of **31**. Displacement ellipsoids are drawn at the 50% probability level. All hydrogen atoms and dichloromethane molecule of crystallization have been omitted for clarity.

The complexes **20**, **22**, **23**, **25**, **26**, **28**, **30** are investigated as catalysts in phospho-aldol addition reaction using diethyl phosphite (Scheme 9, Table 3). The Abramov reaction was carried out in the presence of an amount of catalyst equal to 10 mol%. The maximum ee values were obtained in the case of titanocane **22**.

Using the X-ray analysis data for complexes obtained and also the literature data,[20] one can propose the structure of the catalytic species for compound **22** (Scheme 10). The preferable direction of the attack of the P atom is depicted by the arrow to give the product with (*S*)-configuration.

To investigate the influence of the structure of dialkyl phosphite on the yield and ee values of the products, we carried out the Abramov reaction with dimethyl and diisopropyl phosphites using **22** as a catalyst (Scheme 9, Table 4). From the data obtained it is evident that the increase of the steric volume of substituents in $HP(O)(OR)_2$ results in increase of ee value from 16 to 56%. At the same time there is no reaction in the case of bulky derivatives such as di(1-adamanthyl)phosphite.

Compounds **39**–**41** are novel. The absolute stereochemistry of these derivatives was determined by ^1H and ^{31}P NMR spectroscopy using the analysis of their esters with *O*-acetyl-



Scheme 9 Enantioselective additions of dialkyl phosphites to aromatic aldehydes catalysed by **20**, **22**, **23**, **25**, **26**, **28**, **30**.

Table 3 Enantioselective additions of diethyl phosphite to aromatic aldehydes catalysed by **20**, **22**, **23**, **25**, **26**, **28** and **30**

Ar	R	Complex	Yield (%)	ee (%)	Product
Ph	Et	**20**	84	24	(*S*)-(−)-**32**
	Et	**22**	83	38	(*S*)-(−)-**32**
	Et	**23**	81	24	(*R*)-(+)-**32**
	Et	**25**	82	30	(*R*)-(+)-**32**
	Et	**26**	78	20	(*S*)-(−)-**32**
	Et	**28**	74	10	(*S*)-(−)-**32**
	Et	**30**	78	28	(*R*)-(+)-**32**
3-$O_2NC_6H_4$	Et	**22**	74	28	(*S*)-(−)-**33**
	Et	**30**	72	10	(*R*)-(+)-**33**
4-$MeOC_6H_4$	Et	**22**	81	34	(*S*)-(−)-**34**
	Et	**30**	56	12	(*R*)-(+)-**34**

Table 4 Enantioselective additions of dimethyl and diisopropyl phosphites to aromatic aldehydes catalysed by **22**, **29**

Ar	R	Product	Complex	ee (%)	Yield (%)
Ph	Me	(*S*)-(−)-**35**	**22**	16	73
Ph	*i*-Pr	(*S*)-(−)-**36**	**22**	50	81
Ph	*i*-Pr	(*S*)-(−)-**36**	**29**	46	73
2-BrC_6H_4	*i*-Pr	(*S*)-(−)-**37**	**22**	14	84
4-$MeOC_6H_4$	*i*-Pr	(*S*)-(−)-**38**	**22**	35	68
3-$O_2NC_6H_4$	*i*-Pr	(*S*)-(−)-**39**	**22**	52	76
4-FC_6H_4	*i*-Pr	(*S*)-(−)-**40**	**22**	40	76
	*i*-Pr	(*S*)-(−)-**41**	**22**	56	68

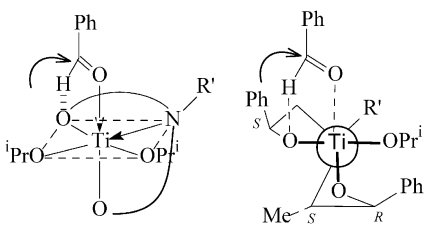
(*S*)-(+)-mandelic acid **8** (Scheme 11).[13a,21] Chemical shifts of the protons for AcOC*H* group and ^{31}P NMR spectra are summarised in Table 5.

In all cases δ values for the major isomers due to shielding effect of aromatic groups were observed at higher field compared to those arising from the minor enantiomers. On the basis of these arguments the signals of the major isomer are assigned to be from the esters derived from the α-hydroxy phosphonates with (*S*)-configuration. Therefore, the absolute configuration of the **39–41** was unambiguously determined to be (*S*).

Experimental

General comments

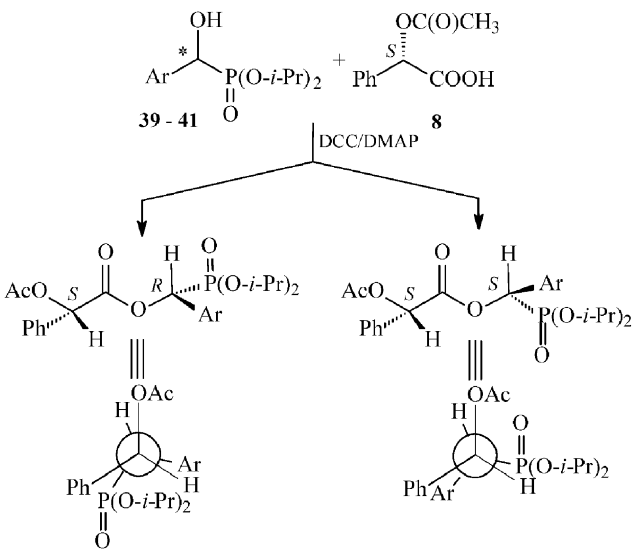
All manipulations with titanium compounds were carried out under an argon atmosphere using standard Schlenk techniques. Solvents were dried by standard methods and distilled before use. Ti(O-*i*-Pr)$_4$ (Aldrich) was distilled before use. (*R*)-(+)-1-Phenylethylamine **1** (Merck), (1*R*,2*S*)-(−)-ephedrine **2** (Aldrich), (*S*)-(−)-α,α-diphenylprolinol **3** (Merck), isobutylene oxide **4** (Acros), (*R*)-styrene oxide **6** (Acros), (1*S*)-(+)-camphor-10-sulfonic acid monohydrate **7** (Merck), (1*R*,2*S*,5*R*)-(−)-menthol (Acros) were used as supplied. 2,2-Diphenyloxirane **5**,[22] *O*-acetyl-(*S*)-(+)-mandelic acid **8**,[23] dimethyl-, diethyl- and di(isopropyl)phosphite,[24] (1-adamanthyl)phosphite,[25] di-(1*R*,2*S*,5*R*)-menthyl chlorophosphite[26] were synthesized according to the literature procedure. $C_6D_5CD_3$, $CDCl_3$ were obtained from Deutero GmbH. ^1H (400 MHz), ^{13}C (100 MHz) and ^{31}P (160 MHz) spectra were recorded at 295 K (unless otherwise stated) on a Bruker Avance 400 spectrometer using the residual solvent resonance for ^1H and ^{13}C and 85% H_3PO_4 for ^{31}P as standards. *J* Values are given in Hz. ^{13}C NMR spectra were ^1H decoupled. Mass spectra (EI-MS) were recorded on a VARIAN CH-7a device using electron impact ionization at 70 eV; all assignments were made with reference to the most abundant isotopes. Mass spectra (ESI) were recorded in acetonitrile for positive ions. Elemental analyses were carried out by the Microanalytical Laboratory of the Chemistry Department of the Moscow State University. Optical rotations were measured with an EPO-1 polarimeter in a 0.250-dm^3 cell and are recorded in units of 10^{-1} deg cm^2 g^{-1}. Enantiomeric excess (ee) values of dialkyl hydroxy(aryl) methylphosphonates **32–41** is assumed equal to the percent de calculated from integration of the ^{31}P NMR downfield spectral signals (Table 6) of the diastereomeric esters formed upon treatment with di-(1*R*,2*S*,5*R*)-menthyl chlorophosphite.[26] Absolute configuration of the known dialkyl hydroxy(aryl)methylphosphonates was established according to the optical rotations of the samples according to literature data.[18] Catalytic reactions were monitored by TLC using Silufol UV-254 plates. Flash chromatography was performed as described.[27]



Scheme 10 Schematic representation of possible catalytic species for Abramov reaction in the case of **22**.

Syntheses of ligand precursors

2-Methyl-1-{[(1*R*)-1-phenylethyl]amino}propan-2-ol, (*R*)-PhCH(Me)N(H)(CH$_2$C(Me)$_2$OH) (9). A mixture of **1** (7.99 g, 65.9 mmol) and isobutylene oxide **4** (5.23 g, 72.5 mmol) was heated at 90 °C for 260 h in the Schlenk tube equipped with a J. Young valve. The residue was distilled *in vacuo* to give **9** as a



Scheme 11 Identification of absolute stereochemistry of diisopropyl α-hydroxy phosphonates **39–41** using *O*-acetyl-(*S*)-(+)-mandelic acid **8**.

Table 5 ^{1}H for AcOC*H* group and ^{31}P NMR data of *O*-acetyl-(*S*)-(+)-mandelic acid esters of **39–41**

	O-acetyl-(*S*)-(+)-mandelic acid esters			
	$\delta(^{31}P)$/ppm		$\delta(^{1}H)$/ppm	
Chiral phosphonate	Major	Minor	Major	Minor
(*S*)-(−)-**39**	12.80	12.67	5.99	5.97
(*S*)-(−)-**40**[a]	14.37	14.15	5.95	5.92
(*S*)-(−)-**41**	13.01	12.72	5.94	5.91

[a] $-J_{PF}$ 4.0 Hz for the (*S*,*R*)-diastereomer; J_{PF} 5.9 Hz for the (*S*,*S*)-diastereomer.

colorless oil (9.41 g, 74%), which solidified on standing forming a white solid; mp 37–38 °C; bp 106–108 °C (*ca.* 0.6 Torr); $[\alpha]_D^{22}$ +49.7 (*c* 10.0 in EtOH); $C_{12}H_{19}NO$ requires C, 74.6; H, 9.9; N, 7.25%; found C, 74.4; H, 10.1; N, 7.5%; δ_H (400.1 MHz, $CDCl_3$, ppm) 7.38–7.25 (5H, m, CH_{arom}), 3.79 (1H, q, *J* 6.3, NCH), 3.23, 2.16 (br s, each 1H, OH, NH), 2.47 (1H, d, *J* 11.7, NC(*H*)(H)), 2.39 (1H, d, *J* 11.7, NC(H)(*H*)), 1.40 (3H, d, *J* 6.3, CHC*H*$_3$), 1.20, 1.17 (s, each 3H, 2CH$_3$); δ_C (100.61 MHz, $CDCl_3$, ppm) 145.48, 128.32, 126.77, 126.27 (C_{arom} and CH_{arom}), 69.10 (*C*Me$_2$), 58.46, 57.97 (NCH_2, NCH), 23.78, 27.11 (C(*C*H$_3$)$_2$), 24.28 (CH*C*H$_3$).

1-{(2-Hydroxy-2-methylpropyl)[(1*R*)-1-phenylethyl]amino}-2-methylpropan-2-ol, (*R*)-PhCH(Me)N(CH$_2$C(Me)$_2$OH)$_2$ (10). A mixture of **1** (3.00 g, 24.8 mmol) and isobutylene oxide **4** (3.93 g, 54.5 mmol) was heated at 90 °C (oil bath) for 380 h in the Schlenk tube equipped with a J. Young valve. The residue was recrystallized from hexane and dried *in vacuo* to give **10** as a white solid (5.56 g, 86%); mp 91–92 °C (from hexane); $[\alpha]_D^{22}$ −9.1 (*c* 4.0 in EtOH); $C_{16}H_{27}NO_2$ requires C, 72.4; H, 10.25; N 5.3%; found C, 72.65; H, 10.4; N, 5.2%; δ_H (400.1 MHz, $CDCl_3$, ppm) 7.41–7.22 (5H, m, CH_{arom}), 4.03–3.98 (3H, m, NCH, 2OH), 2.68 (2H, d, *J* 14.2, NCH_2), 2.59 (2H, d, *J* 14.2, NCH_2), 1.41 (3H, d, *J* 6.8, HCC*H*$_3$), 1.21, 1.04 (s, each 6H, 2C(CH$_3$)$_2$); δ_C (100.61 MHz, $CDCl_3$, ppm) 142.72, 128.20, 127.95, 126.90 (C_{arom} and CH_{arom}), 71.16 (*C*Me$_2$), 63.57 (NCH_2), 62.61 (NCH), 28.25, 27.97 (C(*C*H$_3$)$_2$), 13.77 (HC*C*H$_3$); *m*/*z* (EI) 206 ([M − H − Me$_2$CO]$^+$, 24%), 146 (1), 128 (2), 105 (100), 77 (4).

1-{[(2*R*)-(2-Hydroxy-2-phenylethyl][(1*R*)-1-phenylethyl]amino}-2-methylpropan-2-ol, (*R*)-PhCH(Me)N(CH$_2$C(Me)$_2$OH)((*R*)-CH$_2$CH(Ph)OH) (11). A mixture of **11** (2.41 g, 12.5 mmol) and (*R*)-styrene oxide **6** (1.50 g, 12.5 mmol) was heated at 80 °C for 160 h. The residue was recrystallized from the hexane–ether mixture at −20 °C to give **11** as a white solid (3.40 g, 87%); $[\alpha]_D^{22}$ = −71.4 (*c* 1.4 in EtOH); $C_{20}H_{27}NO_2$ requires C, 76.6; H, 8.7; N, 4.5%; found C, 76.6; H, 8.6; N, 4.4; δ_H (400.1 MHz, $CDCl_3$, ppm) 7.48–7.44 (2H, m, CH_{arom}), 7.37–7.33 (2H, m, CH_{arom}), 7.31–7.20 (6H, m, CH_{arom}), 4.72 (1H, dd, *J* 10.4 and 2.8, OCHPh), 4.10 (1H, q, *J* 6.8, NCH), 3.93, 3.17 (br s, each 1H, 2OH), 2.84–2.79 (1H, m, NC(*H*)(H)), 2.70–2.62 (2H, m, NCH_2), 2.55 (1H, d, *J* 6.6, NC(H)(*H*)), 1.39 (3H, d, *J* 6.8, HCC*H*$_3$), 1.19, 1.04 (s, each 3H, C(C*H*$_3$)$_2$); δ_C (100.61 MHz, $CDCl_3$, ppm) 143.09, 142.55, 128.24, 127.98, 127.37, 126.98, 125.97 (C_{arom} and CH_{arom}), 72.08 (O*C*Me$_2$), 71.28 (O*C*HPh), 61.82, 60.81 (2NCH_2), 60.50 (NCH), 28.15, 27.52 (C(*C*H$_3$)$_2$), 12.25 (HC*C*H$_3$); a signal of one aromatic carbon was not found due to coalescence of two signals.

(1*R*,2*S*)-2-[(2-Hydroxy-2-methylpropyl)(methyl)amino]-1-phenylpropan-1-ol, MeN((*S*)-CH(Me)-(*R*)-CH(Ph)OH)(CH$_2$C(Me)$_2$OH) (12). A mixture of **2** (4.95 g, 30.0 mmol) and isobutylene oxide **4** (2.59 g, 36.0 mmol) was heated at 80 °C for 76 h in the Schlenk tube equipped with a J. Young valve. Volatiles were removed under reduced pressure to give **12** as a yellowish oil. The crude product (7.10 g, 100%) was used without additional purification; $[\alpha]_D^{22}$ −20.0 (*c* 1.0 in EtOH); $C_{14}H_{23}NO_2$ requires C, 70.85; H, 9.8; N, 5.9%; found C, 70.8; H, 9.95; N, 5.7%; δ_H (400.1 MHz, $CDCl_3$, ppm) 7.28–7.10 (5H, m, CH_{arom}), 6.05 (1H, br s, OH), 4.55 (1H, d, *J* 6.8, OCHPh), 2.75–2.67 (1H, m, NCH), 2.44 (1H, br s, OH), 2.26 (2H, br s, NCH_2), 2.18 (3H, s, NCH_3), 0.95 (3H, d, *J* 6.6, CHC*H*$_3$), 0.89, 0.88 (6H, each s, C(C*H*$_3$)$_2$); δ_C (100.61 MHz, $CDCl_3$, ppm) 143.35, 128.18, 127.52, 126.23 (C_{arom} and CH_{arom}), 76.25 (OCH), 70.29 (O*C*Me$_2$), 66.98 (NCH_2), 66.76 (NCH), 40.07 (NCH_3), 27.72, 27.39 (C(*C*H$_3$)$_2$), 9.48 (HC*C*H$_3$); *m*/*z* (EI) 236 ([M − H]$^+$, 10%), 178 (4), 130 (81), 117 (4), 112 (8), 105 (11), 84 (4), 77 (9), 72 (13), 71 (13).

(1*R*,2*S*)-2-[(2-Hydroxy-2,2-diphenylethyl)(methyl)amino]-1-phenylpropan-1-ol, MeN((*S*)-CH(Me)-(*R*)-CH(Ph)OH)-(CH$_2$C(Ph)$_2$OH) (13). A mixture of **2** (4.00 g, 24.2 mmol) and 2,2-diphenyloxirane **5** (4.75 g, 24.2 mmol) was heated at 90 °C for 135 h. The residue was recrystallized from a

Table 6 ^{31}P NMR data of di-(1*R*,2*S*,5*R*)-menthyl phosphite esters of chiral phosphonates (*S*)-(−)-**32** – (*S*)-(−)-**41**

	Minor diastereomer		Major diastereomer		
Chiral phosphonate	$\delta(^{31}P^{III})$/ppm	$\delta(^{31}P^{IV})$/ppm	$\delta(^{31}P^{III})$/ppm	$\delta(^{31}P^{IV})$/ppm	J_{PP}/Hz
(*S*)-(−)-**32**	146.15	19.55	144.10	19.64	17.8
(*S*)-(−)-**33**	145.44	18.05	144.70	18.10	15.9
(*S*)-(−)-**34**	146.31	19.83	143.85	19.91	19.2
(*S*)-(−)-**35**	146.05	21.81	144.12	21.91	17.8
(*S*)-(−)-**36**	146.37	17.95	144.69	18.02	19.8
(*S*)-(−)-**37**	145.82	17.55	143.62	17.63	19.2
(*S*)-(−)-**38**	146.58	18.19	144.59	18.27	20.8
(*S*)-(−)-**39**	145.60	16.21	145.41	16.26	17.8
(*S*)-(−)-**40**	146.41	17.67[a]	144.86	17.61[a]	19.2[a]
(*S*)-(−)-**41**	146.09	16.22	144.61	16.36	19.2

[a] J_{PF} = 4.8 Hz.

hexane–ether mixture at −20 °C to give **13** as a white solid (7.00 g, 81%); mp 87–88 °C; $[\alpha]_D^{22}$ +29.1 (*c* 1.0 in EtOH); $C_{24}H_{27}NO_2$ requires C, 79.7; H, 7.5; N, 3.9%; found C, 79.6; H, 7.4; N, 3.8%; δ_H (400.1 MHz, $CDCl_3$, ppm) 7.31–7.01 (15H, m, CH_{arom}), 4.51 (1H, d, *J* 6.8, OCHPh), 4.36 (1H, br s, OH), 3.24 (1H, d, *J* 13.2, NC(*H*)(H)), 3.17 (1H, d, *J* 13.2, NC(H)(*H*)), 2.76–2.65 (1H, m, NCH), 2.17 (1H, br s, OH), 1.81 (3H, s, NCH_3), 1.00 (3H, d, *J* 6.6, $CHCH_3$); δ_C (100.61 MHz, $CDCl_3$, ppm) 147.11, 146.77, 143.12, 128.43, 128.05, 127.92, 127.74, 126.58, 126.36, 126.22, 125.84, 125.73 (C_{arom} and CH_{arom}), 76.48 (OCHPh), 74.64 (CPh_2), 66.19 (NCH_2), 65.91 (NCH), 38.61 (NCH_3), 9.56 ($HCCH_3$); *m*/*z* (EI) 360 ($[M - H]^+$, 3%), 285 (1), 255 (51), 211 (12), 179 (100).

(1*R*,2*S*)-2-{[(2*R*)-(2-Hydroxy-2-phenylethyl)](methyl)amino}-1-phenylpropan-1-ol, MeN((*S*)-CH(Me)-(*R*)-CH(Ph)OH)((*R*)-CH_2CH(Ph)OH) (14), and (*R*,2*S*)-2-{[(1*S*)-(2-hydroxy-1-phenylethyl)](methyl)amino}-1-phenylpropan-1-ol, MeN((*S*)-CH(Me)-(*R*)-CH(Ph)OH)((*S*)-CH(Ph)CH_2OH) (15). A mixture of **2** (2.06 g, 12.5 mmol) and (*R*)-styrene oxide **6** (1.50 g, 12.5 mmol) was heated at 80 °C for 65 h. Volatiles were removed under reduced pressure to give **14** and **15** as a colorless oil. The approximate ratio of isomers is **14** : **15** = 9 : 1 (according to ^{1}H NMR). The crude product (3.51 g, 98%) was used without additional purification; $[\alpha]_D^{22}$ −71.4 (*c* 1.4 in EtOH); $C_{18}H_{23}NO_2$ requires C, 75.8; H, 8.1; N, 4.9%; found C, 76.0; H, 8.05; N, 4.7%. Spectroscopic data for **14**: δ_H (400.1 MHz, $CDCl_3$, ppm) 7.38–7.22 (10H, m, CH_{arom}), 4.61 (1H, d, *J* 6.8, OC*H*CH), 4.48 (1H, dd, *J* 10.4 and 2.8, OC*H*CH_2), 3.02 (2H, br s, 2OH), 2.86–2.80 (1H, m, NCH), 2.65–2.61 (1H, m, C(*H*)(H)), 2.46–2.41 (1H, m, C(H)(*H*)), 2.24 (3H, s, NCH_3), 1.09 (3H, d, *J* 6.8, $CHCH_3$); δ_C (100.61 MHz, $CDCl_3$, ppm) 143.38, 142.06, 128.30, 128.14, 127.55, 127.28, 126.11, 125.79 (C_{arom} and CH_{arom}), 75.56, 69.43 (OCH), 65.98, 64.95 (NCH, NCH_2), 35.41 (NCH_3), 10.15 ($HCCH_3$). Spectroscopic data for **15**: δ_H (400.1 MHz, $CDCl_3$, ppm) 4.54 (1H, d, *J* 5.8, OCHPh), 3.77–3.72 (1H, m, OC(*H*)(H)), 3.67–3.64 (1H, m, OC(H)(*H*)), 3.55–3.50 (1H, m, NCHPh), 3.07–3.02 (1H, m, NC*H*Me), 2.28 (3H, s, NCH_3), 0.68 (3H, d, *J* 6.8, $CHCH_3$); other proton resonances could not be located due to the overlap with those for major isomer; δ_C (100.61 MHz, $CDCl_3$, ppm) 128.20, 128.00, 126.38 (C_{arom} and CH_{arom}), 75.62, 67.70 (N*C*HPh, O*C*HPh), 61.50 (OCH_2), 58.07 (N*C*HMe), 11.00 ($HCCH_3$); other signals could not be located due to the overlap with those for major isomer or due to the low concentration in the sample.

1-{(2*S*)-2-[Hydroxy(diphenyl)methyl]pyrrolidin-1-yl}-2-methylpropan-2-ol, (*S*)-2-CPh_2OH-*cyclo*-$C_4H_7N(CH_2C(Me)_2OH)$ (16). A mixture of **3** (1.55 g, 6.1 mmol) and isobutylene oxide **4** (0.68 g, 9.4 mmol) was heated at 90 °C for 140 h in the Schlenk tube equipped with a J. Young valve. The residue was recrystallized from a hexane–ether mixture at −20 °C to give **16** as a white solid (1.67 g, 84%); $[\alpha]_D^{22}$ −22.6 (*c* 3.0 in $CHCl_3$); $C_{21}H_{27}NO_2$ requires C, 77.5; H, 8.4; N, 4.3%; found C, 77.5; H, 8.3; N, 4.3%; δ_H (400.1 MHz, $CDCl_3$, ppm) 7.66–7.62 (2H, m, CH_{arom}), 7.54–7.50 (2H, m, CH_{arom}), 7.29–7.21 (4H, m, CH_{arom}), 7.16–7.08 (2H, m, CH_{arom}), 4.81 (1H, br s, OH), 3.99–3.94 (1H, m, NCH), 3.34–3.28, 2.56–2.48 (each 1H, each m, NCH_2), 2.34, 2.27 (each 1H, each d, *J* 13.4, N*C*$H_2$$CMe_2$), 1.83–1.74 (1H, m, C(*H*)(H)), 1.67–1.55 (3H, m, C(*H*)(H), CH_2), 1.12 (1H, br s, OH), 0.89, 0.86 (s, each 3H, $C(CH_3)_2$); δ_C (100.61 MHz, $CDCl_3$, ppm) 147.70, 146.50, 128.07, 127.92, 126.46, 126.14, 125.14 (C_{arom} and CH_{arom}), 77.97 (Ph_2COH), 73.05 ($OCMe_2$), 71.27, 68.47, 58.37 (NCH, $2NCH_2$), 28.99, 28.78 ($C(CH_3)_2$), 27.43, 25.03 ($2CH_2$); a signal of aromatic carbon was not found due to coalescence of two signals; *m*/*z* (EI) 292 ($[M - H_2O - Me]^+$, 1%), 266 (1), 248 (1), 236 (1), 230 (1), 182 (1), 142 (100), 105 (10), 84 (10).

2-{(2*S*)-2-[Hydroxy(diphenyl)methyl]pyrrolidin-1-yl}-1,1-diphenethanol, (*S*)-2-CPh_2OH-*cyclo*-$C_4H_7N(CH_2C(Ph)_2OH)$ (17). A mixture of **3** (1.37 g, 5.4 mmol) and 2,2-diphenyloxirane **5** (1.06 g, 5.4 mmol) was heated at 100 °C for 250 h. The residue was recrystallized from a hexane–ether mixture at −20 °C to give **17** as a white solid (1.92 g, 79%); mp 162–163 °C; $[\alpha]_D^{22}$ −8.2 (*c* 3.2 in $CHCl_3$); $C_{31}H_{31}NO_2$ requires C, 82.8; H, 6.95; N, 3.1%; found C, 82.9; H, 7.25; N, 3.0%; δ_H (400.1 MHz, $CDCl_3$, ppm) 7.73–6.95 (20H, m, CH_{arom}), 4.21–4.16 (2H, m, NCH, OH), 3.38 (1H, d, *J* 14.2, NC(*H*)(H)CPh_2), 3.32 (1H, d, *J* 14.2, NC(H)(*H*)CPh_2), 3.18 (1H, br s, OH), 2.73–2.65 (1H, m, C(*H*)(H)), 2.26–2.17 (1H, m, C(H)(*H*)), 1.92–1.83 (1H, m, C(*H*)(H)), 1.73–1.65 (1H, m, C(H)(*H*)), 1.59–1.54 (1H, m, C(*H*)(H)), 1.52–1.56 (1H, m, C(H)(*H*)); δ_C (100.61 MHz, $CDCl_3$, ppm) 147.30, 146.42, 145.88, 145.76, 128.45, 127.93, 127.84, 127.71, 126.81, 126.72, 126.57, 126.37, 126.29, 126.25, 126.13, 125.57 (C_{arom} and CH_{arom}), 78.45, 76.82 (Ph_2COH), 72.35, 67.74, 57.35 (NCH, $2NCH_2$), 28.76, 24.86 ($2CH_2$); *m*/*z* (EI) 266 ($[M - Ph - PhCHO]^+$, 100%), 197 (3), 183 (6), 105 (93), 77 (50).

General procedure for ^{1}H NMR determination of enantiomeric purity of chiral dialkanolamines 9–17. Chiral solvating agent **7** or **8** (0.09 mmol) was added to the solution of the corresponding chiral dialkanolamine (0.06 mmol) in appropriate deuterated solvent (0.6 mL). The obtained homogeneous solution was analysed by NMR spectroscopy.

Syntheses of complexes

(*R*)-PhCH(Me)N($CH_2C(Me)_2O)_2$Ti(O-*i*-Pr)$_2$ (18). Ti(O-*i*-Pr)$_4$ (1.05 mL, 3.5 mmol) was added dropwise to a stirred solution of dialkanolamine **10** (0.93 g, 3.5 mmol) in chloroform (20 mL). After 7 h refluxing, the solvent was evaporated under reduced pressure. The residue was recrystallized at −20 °C from a toluene–heptane mixture (1 : 1) to give **18** as a white solid (1.40 g, 95%); $C_{22}H_{39}NO_4Ti$ requires C, 61.5; H, 9.15; N, 3.3%; found C, 61.1; H, 9.0; N, 3.0%; δ_H (400.1 MHz, $CDCl_3$, ppm) 7.35–7.23 (5H, m, CH_{arom}), 4.69 (2H, sept, *J* 6.1, OC*H*CH_3), 4.55 (1H, q, *J* 6.7, NCH), 3.06 (2H, br s, 2NC(*H*)(H)), 2.72 (2H, d, *J* 13.4, 2NC(H)(*H*)), 1.69 (3H, d, *J* 6.7, NCHCH_3), 1.49 (6H, br s, OC(Me)CH_3), 1.28, 1.25 (12H, each d, *J* 6.1, OCHCH_3), 1.09 (6H, br s, OC(Me)CH_3); δ_C (100.61 MHz, $CDCl_3$, ppm) 142.38, 128.81, 128.45, 127.45 (C_{arom} and CH_{arom}), 81.61 ($OCMe_2$), 77.20, 76.19 (OCHCH$_3$), 66.00, 64.55 (NCH, NCH_2), 31.26, 30.88 ($OC(CH_3)_2$), 26.05, 25.91 (OCHCH_3), 22.47 (NCHCH_3).

(*R*)-PhCH(Me)N($CH_2C(Me)_2O$)((*R*)-CH_2CH(Ph)O)Ti(O-*i*-Pr)$_2$ (19). Analogously to **18**, complex **19** was prepared from Ti(O-*i*-Pr)$_4$ (0.95 mL, 3.2 mmol) and dialkanolamine **11**

(0.99 g, 3.2 mmol) in chloroform (20 mL). The product was isolated after recrystallization at −20 °C from hexane as a white solid (1.33 g, 88%); $C_{26}H_{39}NO_4Ti$ requires C, 65.4; H, 8.2; N, 2.9%; found C, 64.9; H, 7.9; N, 2.7%; δ_H (400.1 MHz, $CDCl_3$, ppm) 7.30–7.12 (10H, m, CH_{arom}), 5.70–5.61 (1H, m, OCHPh), 4.75 (2H, br s, OC*H*CH_3), 4.46–4.41 (1H, m, NCH), 3.51, 2.53 (each 1H, each br s, NCH_2), 2.94–2.87, 2.82–2.76 (each 1H, each m, NCH_2), 1.81 (3H, d, *J* 4.1, CHC*H*$_3$), 1.34–1.21 (15H, m, CH_3), 1.15 (3H, s, CH_3); δ_C (100.61 MHz, $CDCl_3$, ppm) 144.45, 140.36, 128.81, 128.12, 127.98, 127.58, 126.76, 124.91 (C_{arom} and CH_{arom}), 83.33 (OCHPh), 81.23 (O*C*Me$_2$), 76.68, 76.60, 75.95 (2OCH, NCH), 66.60, 63.68 (2NCH_2), 32.43 (CH*C*H$_3$), 30.79 (OC(Me)*C*H$_3$), 26.15, 26.02, 25.89, 25.77 (2OCH(*C*H$_3$)$_2$), 20.71 (OC(Me)*C*H$_3$).

MeN($CH_2C(Me)_2O$)((*S*)-CH(Me)-(*R*)-CH(Ph)O)Ti(O-*i*-Pr)$_2$ (20). Analogously to **18**, complex **20** was prepared from Ti(O-*i*-Pr)$_4$ (1.15 mL, 3.8 mmol) and dialkanolamine **12** (0.91 g, 3.8 mmol) in chloroform (20 mL). The product (1.53 g, 100%) was isolated as a yellowish oil. ^{1}H NMR spectroscopy of **20** indicated it is a mixture of two diastereomers (**20a**, **20b**) with approximate ratio **20a** : **20b** equal to 55 : 45 ($CDCl_3$) or 52 : 48 ($C_6D_5CD_3$); δ_H (400.1 MHz, $C_6D_5CD_3$, 100 °C, ppm) 7.33 (3H, br s, CH_{arom}), 7.14 (2H, br s, CH_{arom}), 5.59 (1H, br s, OCHPh), 4.79 (2H, br s, 2OC*H*CH_3), 3.02 (1H, br s, NCH), 2.73–2.55 (2H, m, NCH_2), 2.47 (3H, br s, NCH_3), 1.38–1.12 (18H, m, 4OCHC*H*$_3$, OC(Me)$_2$), 0.78 (3H, br s, C*H*$_3$CH). Spectroscopic data for **20a**: δ_H (400.1 MHz, $CDCl_3$, ppm) 7.38–7.31 (2H, m, CH_{arom}), 7.27–7.18 (2H, m, CH_{arom}), 7.16–7.09 (1H, m, CH_{arom}), 5.61 (1H, d, *J* 4.6, OCHPh), 4.77–4.69 (2H, m, 2OC*H*CH_3), 3.30–3.22 (1H, m, NCH), 3.15, 2.63 (2H, each d, *J* 12.9, NCH_2), 2.40 (3H, s, NCH_3), 1.37 (3H, s, OC(Me)C*H*$_3$), 1.22–1.14 (15H, m, 4OCHC*H*$_3$, OC(C*H*$_3$)Me), 0.97–0.88 (3H, m, C*H*$_3$CH); δ_H (400.1 MHz, $C_6D_5CD_3$, ppm) 7.43–7.38 (1H, m, CH_{arom}), 7.32–7.28 (1H, m, CH_{arom}), 7.19–7.12 (2H, m, CH_{arom}), 7.05–7.00 (1H, m, CH_{arom}), 5.72 (1H, d, *J* 4.3, OCHPh), 4.87–4.75 (2H, m, 2OC*H*CH_3), 2.85–2.76 (1H, m, NCH), 2.96 (1H, d, *J* 12.6, NC(*H*)(H)), 2.30 (3H, c, NCH_3), 2.21 (1H, d, *J* 12.6, NC(H)(*H*)), 1.36–1.28 (15H, m, 4OCHC*H*$_3$, OC(Me)C*H*$_3$), 1.11 (3H, c, OC(Me)C*H*$_3$), 0.74 (3H, d, *J* 6.8, C*H*$_3$CH); δ_C (100.61 MHz, $CDCl_3$, ppm) 142.60, 127.45, 126.36, 126.14 (C_{arom} and CH_{arom}), 84.59 (OCHPh), 81.87 (O*C*(CH$_3$)$_2$), 76.68, 76.37 (O*C*HCH$_3$), 71.89, 69.81 (2NCH_2), 43.88 (NCH_3), 31.50, 30.93 (OC(*C*H$_3$)$_2$), 26.35, 26.19, 25.86, 25.79 (4OCH*C*H$_3$), 9.86 (NCH*C*H$_3$). Spectroscopic data for **20b**: δ_H (400.1 MHz, $CDCl_3$, ppm) 5.39 (1H, d, *J* 6.1, OC*H*Ph), 4.70–4.59 (2H, m, OC*H*CH_3), 3.40–3.32 (1H, m, NCH), 2.76 (3H, c, NCH_3), 2.14 (1H, d, *J* 12.9, NC*H*(H)), 1.34 (3H, s, OC(C*H*$_3$)(Me)), 1.25 (3H, s, OC(Me)(C*H*$_3$)), 1.31–1.26 (12H, m, 4OCHC*H*$_3$); other signals could not be located due to the overlap with those for the major isomer; δ_H (400.1 MHz, $C_6D_5CD_3$, ppm) 5.27 (1H, d, *J* 6.1, OCHPh), 4.94–4.86 (2H, m, 2OC*H*CH_3), 3.09–2.99 (1H, m, NCH), 2.67 (1H, d, *J* 12.9, NC(*H*)(H)), 2.52 (3H, s, NCH_3), 1.76 (1H, d, *J* 12.9, NC(H)(*H*)), 1.45–1.36 (15H, m, 4OCHC*H*$_3$, OC(Me)C*H*$_3$), 0.98 (3H, s, OC(C*H*$_3$)Me), 0.65 (3H, d, *J* 7.1, C*H*$_3$CH); δ_C (100.61 MHz, $CDCl_3$, ppm) 142.11, 127.40, 126.80, 126.63 (C_{arom} and CH_{arom}), 86.13 (OCHPh), 81.54 (O*C*(CH$_3$)$_2$), 76.45, 75.99 (O*C*HCH$_3$), 69.77, 65.15 (2NCH_2), 48.83 (NCH_3), 31.06, 30.50 (OC(*C*H$_3$)$_2$), 26.31, 25.80, 25.74 (OCH*C*H$_3$), 9.82 (NCH*C*H$_3$).

MeN($CH_2C(Ph)_2O$)((*S*)-CH(Me)-(*R*)-CH(Ph)O)Ti(O-*i*-Pr)$_2$ (21). Analogously to **18**, complex **21** was prepared from Ti(O-*i*-Pr)$_4$ (0.57 mL, 1.9 mmol) and dialkanolamine **13** (0.69 g, 1.9 mmol) in chloroform (20 mL). The product (0.90 g, 90%) was isolated as a white solid after recrystallization at −20 °C from a dichloromethane–hexane mixture. ^{1}H NMR spectroscopy of **21** in $CDCl_3$ indicated it is a mixture of two diastereomers (**21a**, **21b**) with approximate ratio **21a** : **21b** = 60 : 40. Spectroscopic data for **21a**: δ_H (400.1 MHz, $CDCl_3$, ppm) 7.60–7.52 (4H, m, CH_{arom}), 7.33–6.98 (11H, m, CH_{arom}), 5.59 (1H, d, *J* 6.1, OCHPh), 4.95–4.86 (1H, m, OC*H*CH_3), 4.77–4.70 (1H, m, OC*H*CH_3), 3.98, 3.58 (each 1H, each d, *J* 12.6, NCH_2), 3.28–3.23 (1H, m, NCH), 2.16 (3H, c, NC*H*$_3$), 1.23–1.18 (12H, m, 4OCHC*H*$_3$), 0.85 (3H, d, *J* 6.8, C*H*$_3$CH); δ_H (400.1 MHz, $C_6D_5CD_3$, 100 °C, ppm) 7.59 (6H, br s, CH_{arom}), 7.20 (9H, br s, CH_{arom}), 5.62 (1H, br s, OCHPh), 4.94, 4.76 (each 1H, each br s, 2OC*H*CH_3), 3.92 (1H, br s, NCH), 3.44 (each 1H, each br s, NCH_2), 2.20 (3H, br s, NCH_3), 1.46, 1.25 (each 6H, each br s, 2OCHC*H*$_3$), 0.75 (3H, br s, C*H*$_3$CH); δ_C (100.61 MHz, $CDCl_3$, ppm) 149.70, 148.59, 142.57, 128.20, 127.99, 127.64, 127.00, 126.58, 126.33, 126.16, 125.19, 124.84 (C_{arom} and CH_{arom}), 87.99, 84.45 (O*C*HPh, O*C*Ph$_2$), 77.07 (O*C*HCH$_3$), 69.20, 66.96 (NCH, NCH_2), 42.85 (NCH_3), 26.31, 26.19 (OCH*C*H$_3$), 9.74 (NCH*C*H$_3$). Spectroscopic data for **21b**: δ_H (400.1 MHz, $CDCl_3$, ppm) 7.60–7.52 (4H, m, CH_{arom}), 7.33–6.98 (11H, m, CH_{arom}), 5.33 (1H, d, *J* 6.6, OC*H*Ph), 4.95–4.86, 4.70–4.65 (each 1H, each m, 2OC*H*CH_3), 3.53–3.47 (2H, m, NCH), 3.27–3.24 (1H, m, NCH_2), 2.24 (3H, s, NCH_3), 1.47–1.42 (12H, m, 4OCHC*H*$_3$), 0.98 (3H, d, *J* 6.8, C*H*$_3$CH); δ_H (400.1 MHz, $C_6D_5CD_3$, 100 °C, ppm) 5.32 (1H, br s, OCHPh), 3.57 (1H, br s, NCH), 3.05 (1H, br s, NC*H*(H)), 0.77 (3H, br s, C*H*$_3$CH); other signals could not be located due to the overlap with those for major isomer; δ_C (100.61 MHz, $CDCl_3$, ppm) 149.39, 148.37, 141.32, 128.03, 127.87, 127.33, 126.70, 126.43, 126.27, 126.07 124.96, 124.43 (C_{arom} and CH_{arom}), 87.37, 87.23 (O*C*Ph$_2$, O*C*HPh), 77.20 (O*C*HCH$_3$), 69.43, 64.56 (NCH, NCH_2), 47.82 (NCH_3), 26.39, 26.23 (OCH*C*H$_3$), 9.87 (NCH*C*H$_3$).

MeN((*S*)-CH(Me)-(*R*)-CH(Ph)O)((*R*)-CH_2CH(Ph)O)Ti(O-*i*-Pr)$_2$ (22). Analogously to **18**, complex **22** was prepared from Ti(O-*i*-Pr)$_4$ (0.57 mL, 1.9 mmol) and the mixture of dialkanolamines **14** and **15** (0.52 g, 1.9 mmol) in chloroform (20 mL). The crude product was extracted with pentane. Compound **22** was isolated after recrystallization at −20 °C from hexane as a white solid (0.64 g, 78%); $C_{24}H_{35}NO_4Ti$ requires C, 64.1; H, 7.85; N, 3.1%; found C, 63.6; H, 7.6; N, 3.0%. ^{1}H NMR spectroscopy of **22** in $CDCl_3$ indicated it is a mixture of two diastereomers (**22a**, **22b**) with approximate ratio **22a** : **22b** = 11 : 1. Spectroscopic data for **22a**: δ_H (400.1 MHz, $CDCl_3$, ppm) 7.34–7.18 (10H, m, CH_{arom}), 5.99 (1H, br s, OCHPh), 5.76–5.71 (1H, m, OCHPh), 4.82–4.75 (2H, m, OC*H*CH_3), 3.40–3.34 (1H, m, NCH), 3.08–3.03, 2.83–2.78 (each 1H, each m, NCH_2), 2.66 (3H, s, NCH_3), 1.42–1.35, 1.28–1.23 (each 6H, each m, OCHC*H*$_3$), 0.91 (3H, d, *J* 6.1, NCHC*H*$_3$); δ_C (100.61

MHz, $CDCl_3$, ppm) 143.35, 142.70, 128.11, 127.78, 127.07, 126.38, 125.50, 125.14 (C_{arom} and CH_{arom}), 82.91, 81.27 (OCHPh), 76.88 (O*C*HCH$_3$), 68.39, 66.37 (N*C*HMe, NCH_2), 40.75 (N*C*H$_3$), 25.87 (OCH*C*H$_3$), 11.13 (NCH*C*H$_3$). Spectroscopic data for **22b**: δ_H (400.1 MHz, $CDCl_3$, ppm) 5.01–4.95 (1H, m, OCH), 4.65–4.61, 4.50–4.46, 3.25–3.18 (each 1H, each m, NCH, NCH_2), 2.61 (3H, s, NCH_3), 1.04 (3H, d, *J* 6.1, NCHC*H*$_3$); other signals could not be located due to the overlap with those for major isomer; δ_C (100.61 MHz, $CDCl_3$, ppm) 128.74, 128.42, 124.76 (C_{arom} and CH_{arom}), 84.12 (OCHPh), 76.02 (O*C*HCH$_3$), 26.40, 26.26 (OCH*C*H$_3$); other signals could not be located due to the overlap with those for major isomer or due to the low concentration in the sample.

((*S*)-2-CPh$_2$O)(*cyclo*-C$_4$H$_7$N(CH$_2$C(Me)$_2$O))Ti(O-*i*-Pr)$_2$ (23). Analogously to **18**, complex **23** was prepared from Ti(O-*i*-Pr)$_4$ (0.62 mL, 2.1 mmol) and dialkanolamine **16** (0.67 g, 2.1 mmol) in toluene (20 mL). The crude product was extracted with hexane, solvent was removed under reduced pressure and residue was treated with pentane to give **23** as a white solid (0.73 g, 72%); $C_{27}H_{39}NO_4Ti$ requires C, 66.25; H, 8.0; N, 2.9%; found C, 66.1; H, 7.85; N, 3.2%; δ_H (400.1 MHz, $CDCl_3$, ppm) 7.78–7.73 (2H, m, CH_{arom}), 7.52–7.27, 7.20–7.00 (each 4H, each m, CH_{arom}), 4.97–4.87, 4.76–4.66 (each 1H, each m, 2OC*H*CH$_3$), 4.25–4.10 (2H, m, NCH, NC(*H*)(H)), 2.84, 2.23 (each 1H, each d, *J* 13.2, NC*H*$_2$CO), 2.58–2.53 (1H, m, NC(H)(*H*)), 1.93–1.82, 1.79–1.59 (4H, m, $2CH_2$), 1.53 (3H, d, *J* 14.9, OCHC*H*$_3$), 1.41 (3H, d, *J* 5.3, OCHC*H*$_3$), 1.28–1.12 (9H, m, OC(Me)C*H*$_3$, 2OCHC*H*$_3$), 0.55 (3H, br s, OC(Me)C*H*$_3$); δ_C (100.61 MHz, $CDCl_3$, ppm) 149.59, 149.07, 128.03, 127.60, 126.16, 125.69, 125.37, 125.01 (C_{arom} and CH_{arom}), 88.96 ($OCPh_2$), 81.66 (O*C*Me$_2$), 76.71, 76.66, 76.45 (2OCH, NCH), 69.90, 61.69 (NCH_2), 30.07, 29.62 ($2CH_2$), 28.92, 26.26, 22.24, 26.22, 26.16, 26.13 (2OCH(*C*H$_3$)$_2$, C(*C*H$_3$)$_2$).

(*R*)-PhCH(Me)N(CH$_2$C(Me)$_2$O)$_2$TiCl$_2$*HNMe$_2$ (24). A solution of dialkanolamine **10** (0.93 g, 3.5 mmol) in toluene (20 mL) was added dropwise at −40 °C to a stirred solution of $(Me_2N)_2TiCl_2$ (0.73 g, 3.5 mmol) in toluene (30 mL). The reaction mixture was allowed to warm up to room temperature overnight. The solvent was evaporated under reduced pressure and the product **24** was isolated after recrystallization at −20 °C from dichloromethane–heptane mixture as a yellow solid (1.10 g, 82%); $C_{18}H_{32}Cl_2N_2O_2Ti$ requires C, 50.6; H, 7.55; N, 6.6%; found C, 48.8; H, 7.9; N, 6.60%; δ_H (400.1 MHz, $CDCl_3$, ppm) 7.33–7.21 (5H, m, CH_{arom}), 5.16 (1H, br s, *H*NMe$_2$), 4.07 (1H, q, *J* 6.8, NCH), 3.00, 2.93 (each 2H, each d, *J* 14.9, $2NCH_2$), 2.64 (6H, s, HN(C*H*$_3$)$_2$), 1.56 (3H, d, *J* 6.8, CHC*H*$_3$), 1.30, 1.15 (each 6H, each s, C(C*H*$_3$)$_2$); δ_C (100.61 MHz, $CDCl_3$, ppm) 142.71, 128.40, 128.21, 127.19 (C_{arom} and CH_{arom}), 95.49 (O*C*Me$_2$), 67.58, 65.08 (NCH_2, NCH), 40.03 (HN(*C*H$_3$)$_2$), 27.42, 27.33 (C(*C*H$_3$)$_2$), 16.36 (CH*C*H$_3$); *m*/*z* (EI) 352 ([M − HNMe$_2$ − 2CH$_3$]$^+$, 2%), 295 (1), 206 (18), 105 (100), 83 (25); *m*/*z* (ESI$^+$) 383.2 ([M − HNMe$_2$]$^+$).

[(*R*)-PhCH(Me)N(CH$_2$C(Me)$_2$O)$_2$]$_2$Ti (25). Ti(O-*i*-Pr)$_4$ (0.54 mL, 1.8 mmol) was added dropwise to a stirred solution of dialkanolamine **10** (0.95 g, 3.6 mmol) in toluene (20 mL). After 13 h refluxing, the solvent was evaporated under reduced pressure. The residue was recrystallized from toluene at −20 °C to give **25** as a white solid (0.96 g, 93%); $C_{32}H_{50}N_2O_4Ti$ requires C, 66.9; H, 8.8; N, 4.9%; found C, 67.0; H, 8.6; N, 5.0%; δ_H (400.1 MHz, $CDCl_3$, ppm) 7.35–7.21 (10H, m, CH_{arom}), 4.43 (2H, q, *J* 6.8, 2NCH), 2.87 (4H, br s, $2NCH_2$), 2.61 (4H, d, *J* 6.8, $2NCH_2$), 1.65 (6H, d, *J* 6.8, 2C*H*$_3$CHN), 1.50, 1.08 (each 12H, each s, 4OC(CH$_3$)$_2$); δ_C (100.61 MHz, $CDCl_3$, ppm) 142.92, 128.77, 128.14, 127.04 (C_{arom} and CH_{arom}), 82.23 (*C*Me$_2$O), 64.81 (NCH), 64.04 (NCH_2), 30.34, 29.37 (OC(*C*H$_3$)$_2$), 20.80 (NCH*C*H$_3$); *m*/*z* (ESI$^+$) 575.5 ([M]$^+$).

[(*R*)-PhCH(Me)N(CH$_2$C(Me)$_2$O)((*R*)-CH$_2$CH(Ph)O)]$_2$Ti (26). Analogously to **25**, complex **26** was prepared from Ti(O-*i*-Pr)$_4$ (0.87 mL, 2.9 mmol) and dialkanolamine **11** (1.83 g, 5.8 mmol) in toluene (20 mL). The product **26** was isolated as a white solid after recrystallization at −20 °C from toluene (1.45 g, 74%); $C_{40}H_{50}N_2O_4Ti$ requires C, 71.6; H, 7.5; N, 4.2%; found C, 71.7; H, 7.5; N, 4.0%; δ_H (400.1 MHz, $CDCl_3$, ppm) 7.43–7.12 (20H, m, CH_{arom}), 5.66, 5.56 (each 1H, each dd, *J* 9.6 and 2.8, 2OCHPh), 4.27, 4.22 (each 1H, each d, *J* 6.8, 2NCH), 3.43, 2.90 (each 1H, each d, *J* 13.9, NC*H*$_2$C), 3.30 (1H, d, *J* 13.6, NC*H*(H)C), 2.86–2.75 (3H, m, NCH(*H*)C, NCH_2), 2.65–2.57 (2H, m, NCH_2), 1.68, 1.55 (each 3H, each d, *J* 6.8, 2NCHC*H*$_3$), 1.30, 1.28, 1.26, 1.19 (12H, each s, 2OC(C*H*$_3$)$_2$); δ_C (100.61 MHz, $CDCl_3$, ppm) 144.73, 144.53, 142.49, 142.12, 128.97, 128.56, 128.53, 128.16, 128.05, 128.00, 127.11, 127.00, 126.84, 126.70 (C_{arom} and CH_{arom}), 86.18, 85.17 (2OCHPh), 84.06, 83.60 (2O*C*Me$_2$), 67.46, 67.06 (2NCH), 64.94, 64.73, 64.46 63.08 ($4NCH_2$), 30.92, 30.24, 29.97, 29.47 (2OC(*C*H$_3$)$_2$), 19.56, 18.81 (2NCH*C*H$_3$); signals of two aromatic carbons were not found due to coalescence of signals.

[MeN((*S*)-CH(Me)-(*R*)-CH(Ph)O)(CH$_2$C(Me)$_2$O)]$_2$Ti (27). Analogously to **25**, complex **27** was prepared from Ti(O-*i*-Pr)$_4$ (0.41 mL, 1.4 mmol) and dialkanolamine **12** (0.64 g, 2.8 mmol) in toluene (20 mL). The product **27** was isolated as a white solid after recrystallization at −20 °C from dichloromethane–heptane mixture (0.65 g, 90%). ^{1}H NMR spectroscopy of **27** in $CDCl_3$ indicated it is a mixture of two diastereomers (**27a**, **27b**) with approximate ratio **27a** : **27b** = 3 : 1; $C_{28}H_{42}N_2O_4Ti$ requires C, 64.9; H, 8.2; N, 5.4%; found C, 65.0; H, 8.1; N, 5.3%. Spectroscopic data for **27a**: δ_H (400.1 MHz, $CDCl_3$, ppm) 7.34–7.13 (10H, m, CH_{arom}), 6.07 (2H, br s, 2OCH), 3.29, 2.74 (each 2H, each d, *J* 13.2, $2NCH_2$), 2.88 (2H, br s, 2NCH), 2.81 (6H, br s, $2NCH_3$), 1.71, 1.18 (each 6H, each s, 2C(CH$_3$)$_2$), 0.78 (6H, d, *J* 6.2, 2C*H*$_3$CH); δ_C (100.61 MHz, $CDCl_3$, ppm) 143.96, 127.90, 126.09, 125.34 (C_{arom} and CH_{arom}), 83.69 (OCHPh), 82.70 (*C*Me$_2$), 71.57 (NCH_2), 70.30 (Me*C*H), 45.25 (NCH_3), 30.68, 27.76 (C(*C*H$_3$)$_2$), 10.93 (HC*C*H$_3$). Spectroscopic data for **27b**: δ_H (400.1 MHz, $CDCl_3$, ppm) 1.28 (6H, br s, C(CH$_3$)$_2$), 0.98 (6H, d, *J* 4.7, C*H*$_3$CH); other signals could not be located due to the overlap with those for major isomer; δ_C (100.61 MHz, $CDCl_3$, ppm) 128.18, 127.52, 126.23 (C_{arom} and CH_{arom}), 82.31 (*C*Me$_2$), 66.99 (Me*C*H), 66.73 (CH_2); other signals could not be located due to the overlap with those for major isomer or due to the low concentration in the sample.

[MeN((*S*)-CH(Me)-(*R*)-CH(Ph)O)(CH$_2$C(Ph)$_2$O)]$_2$Ti (28). Analogously to **25**, complex **28** was prepared from Ti(O-*i*-Pr)$_4$ (0.41 mL, 1.4 mmol) and dialkanolamine **13** (1.01 g, 2.8 mmol) in toluene (20 mL). The product **28** was isolated as a white solid after recrystallization at −20 °C from toluene (0.96 g, 91%). ^{1}H NMR spectroscopy of **28** in $CDCl_3$ or $C_6D_5CD_3$ indicated it is a mixture of two diastereomers (**28a**, **28b**) with approximate ratio **28a** : **28b** = 75 : 25; $C_{48}H_{50}N_2O_4Ti$ requires C, 75.2; H, 6.6; N, 3.65%; found C, 75.1; H, 6.2; N, 3.7%; *m*/*z* (EI) 584 ([M − Ph − PhCO]$^+$, 6%), 374 (1), 246 (6), 182 (19), 105 (100), 77 (84), 64 (8); *m*/*z* (ESI$^+$) 767.5 ([M]$^+$). Spectroscopic data for **28a**: δ_H (400.1 MHz, $CDCl_3$, ppm) 7.96–7.01 (30H, m, CH_{arom}), 5.82 (2H, d, *J* 8.1, 2OCH), 4.38, 4.07 (each 2H, each d, *J* 11.3, 2NCH_2), 4.35–4.28 (2H, m, 2NCH), 2.27 (6H, s, 2NCH_3), 0.92 (6H, d, *J* 6.8, 2C*H*$_3$CH); δ_H (400.1 MHz, $C_6D_5CD_3$, ppm) 7.97–6.97 (30H, CH_{arom}), 5.80 (2H, d, *J* 8.1, 2OCH), 4.19, 3.75 (each 2H, each d, *J* 11.1, 2NCH_2), 4.05–3.98 (2H, m, 2NCH), 2.18 (6H, s, 2NCH_3), 0.68 (6H, d, *J* 6.6, 2C*H*$_3$CH); δ_C (100.61 MHz, $CDCl_3$, ppm) 150.93, 149.41, 143.69, 127.97, 127.40, 127.23, 126.25, 126.19, 126.05, 125.90, 125.68, 125.58 (C_{arom} and CH_{arom}), 89.14 (O*C*Ph$_2$), 87.13 (OCH), 74.20 (NCH), 69.46 (NCH_2), 38.48 (NCH_3), 10.78 (HC*C*H$_3$). Spectroscopic data for **28b**: δ_H (400.1 MHz, $CDCl_3$, ppm) 6.16 (1H, br s, OCH), 5.60 (1H, br s, OCH), 4.67, 4.20 (each 1H, each br s, NCH_2), 4.62–4.55 (2H, m, NCH_2), 3.93–3.87 (1H, m, NCH), 3.10 (1H, br s, NCH), 2.70 (3H, s, NCH_3), 2.22 (3H, s, NCH_3), 1.14 (3H, d, *J* 5.8, C*H*$_3$CH), 1.09 (3H, d, *J* 6.6, C*H*$_3$CH); other signals could not be located due to the overlap with those for major isomer; δ_H (400.1 MHz, $C_6D_5CD_3$, ppm) 6.18 (1H, br s, OCH), 5.49 (1H, br s, OCH), 4.49, 4.28 (each 1H, each br s, NCH_2), 3.95–3.84, 3.58–3.50 (each 1H, m, NCH), 2.71 (3H, br s, NCH_3), 2.57 (3H, s, NCH_3), 0.81 (3H, br s, C*H*$_3$CH); other signals could not be located due to the overlap with those for major isomer; δ_C (100.61 MHz, $CDCl_3$, ppm) 151.26, 143.41, 128.50, 128.39, 127.71, 126.92, 126.40, 125.71, 125.08 (C_{arom} and CH_{arom}), 85.60 (OCH), 74.65 (NCH), 65.27 (NCH_2), 36.05 (NCH_3), 11.40 (HC*C*H$_3$); other signals could not be located due to the overlap with those for major isomer or due to the low concentration in the sample.

[MeN((*S*)-CH(Me)-(*R*)-CH(Ph)O)((*R*)-CH$_2$CH(Ph)O)]$_2$Ti (29). Analogously to **25**, complex **29** was prepared from Ti(O-*i*-Pr)$_4$ (0.27 mL, 0.9 mmol) and the mixture of dialkanolamines **14** and **15** (0.51 g, 1.8 mmol) in toluene (15 mL). The crude product was treated with ether. The product **29** was isolated as a white solid after recrystallization at −20 °C from toluene (0.50 g, 90%). ^{1}H NMR spectroscopy of **29** in $CDCl_3$ indicated it is a mixture of two diastereomers (**29a**, **29b**) with approximate ratio **29a** : **29b** = 3 : 1; $C_{36}H_{42}N_2O_4Ti$ requires C, 70.35; H, 6.9; N, 4.6%; found C, 70.1; H, 6.6; N, 4.3%. Spectroscopic data for **29a**: δ_H (400.1 MHz, $CDCl_3$, ppm) 7.58–7.15 (20H, m, CH_{arom}), 6.08 (2H, d, *J* 6.3, 2OC*H*PhCHMe), 5.88 (2H, dd, *J* 10.1 and 2.8, 2OC*H*PhCH$_2$), 3.69–3.61, 3.76–3.72 (each 2H, each m, 2NCH_2), 3.11–2.94 (2H, m, 2NCH), 2.71 (6H, s, 2NCH_3), 0.97 (6H, d, *J* 6.3, C*H*$_3$CH); δ_C (100.61 MHz, $CDCl_3$, ppm) 144.18, 143.53, 128.88, 128.03, 127.53, 126.65, 126.32, 125.67 (C_{arom} and CH_{arom}), 86.20, 82.01 (OCHPh), 68.39, 68.27 (N*C*HMe, NCH_2), 37.64 (NCH_3), 11.12 (NCH*C*H$_3$). Spectroscopic data for **29b**: δ_H (400.1 MHz, $CDCl_3$, ppm) 6.12 (2H, br s, OCH), 5.85–5.79 (2H, m, OCH), 3.45–3.38 (4H, m, 2NCH_2), 2.88–2.76 (8H, m, 2NCH, 2NCH_3), 1.19 (6H, d, *J* 6.1, 2C*H*$_3$CH); other signals could not be located due to the overlap with those for major isomer or due to the low concentration in the sample; δ_C (100.61 MHz, $CDCl_3$, ppm) 143.23, 128.08, 127.91, 127.75, 126.90, 125.97, 125.15 (C_{arom} and CH_{arom}), 84.74 (OCHPh), 68.82 (NCH_2), 40.75 (NCH_3); other signals could not be located due to the overlap with those for major isomer.

[(*S*)-2-CPh$_2$O-*cyclo*-C$_4$H$_7$N(CH$_2$C(Me)$_2$O)]$_2$Ti (30). Analogously to **25**, complex **30** was prepared from Ti(O-*i*-Pr)$_4$ (0.45 mL, 1.5 mmol) and dialkanolamine **16** (0.98 g, 3.0 mmol) in heptane (40 mL). The product **30** was isolated as a white solid after recrystallization at −20 °C from heptane (1.01 g, 96%); $C_{41}H_{48}N_2O_4Ti$ requires C, 72.3; H, 7.1; N, 4.1%; found C, 72.4; H, 7.3; N, 3.9%; δ_H (400.1 MHz, $CDCl_3$, ppm) 8.18, 7.81 (each 4H, each d, *J* 7.6, CH_{arom}), 7.43–7.35, 7.31–7.24 (each 4H, each m, CH_{arom}), 7.22–7.17, 7.15–7.09 (each 2H, each m, CH_{arom}), 4.29–4.22 (2H, m, 2NCH), 4.02–3.94, 2.65–2.56 (each 2H, each m, 2NCH_2), 3.00, 2.23 (each 2H, each d, *J* 12.5, 2NCH_2C), 2.19–2.10, 1.86–1.80, 1.77–1.69, 1.61–1.55 (each 2H, each m, 4CH_2), 1.19, 0.60 (each 6H, each br s, 2OC(C*H*$_3$)$_2$); δ_C (100.61 MHz, $CDCl_3$, ppm) 151.35, 150.37, 127.93, 127.50, 126.17, 125.96, 125.66, 125.47 (C_{arom} and CH_{arom}), 89.70 (OCPh$_2$), 83.04 (O*C*Me$_2$), 75.7, 68.97, 60.43 (NCH, 2NCH_2), 30.86, 30.10 (2CH_2), 29.29, 22.58 (OC(*C*H$_3$)$_2$); *m*/*z* (ESI$^+$) 695.3 ([M]$^+$).

[(*S*)-2-CPh$_2$O-*cyclo*-C$_4$H$_7$N(CH$_2$C(Ph)$_2$O)]$_2$Ti (31). Analogously to **25**, complex **31** was prepared from Ti(O-*i*-Pr)$_4$ (0.60 mL, 2.0 mmol) and dialkanolamine **17** (1.80 g, 4.0 mmol) in toluene (20 mL). The product **31** was isolated as a white solid after recrystallization at −20 °C from toluene (1.70 g, 90%); $C_{62}H_{58}N_2O_4Ti$ requires C, 79.0; H, 6.2; N, 3.0%; found C, 78.6; H, 6.15; N, 3.05%; δ_H (400.1 MHz, $CDCl_3$, ppm) 8.30–8.25, 7.54–7.47 (each 4H, each m, CH_{arom}), 7.38–7.30, 7.25–7.15 (each 8H, each m, CH_{arom}), 7.08–6.90 (12H, m, CH_{arom}), 6.79–6.69 (4H, m, CH_{arom}), 4.30 (2H, dd, *J* 10.1 and 6.1, 2NCH), 4.18, 3.18 (each 2H, each d, *J* 12.1, C*H*$_2$CPh$_2$), 3.70–3.60, 2.24–2.18 (each 2H, each m, 2NCH_2), 1.97–1.85, 1.83–1.73, 1.58–1.50, 1.40–1.31 (each 2H, each m, 4CH_2); δ_C (100.61 MHz, $CDCl_3$, ppm) 151.21, 149.03, 148.10, 148.01, 128.20, 127.46, 127.40, 126.30, 126.25, 126.20, 126.15, 126.01, 125.60, 125.40, 125.28 (C_{arom} and CH_{arom}), 91.26, 90.51 (2Ph$_2$*C*O), 75.81 (NCH), 69.12, 59.03 (2NCH_2), 28.63, 21.86 (2CH_2); a signal of aromatic carbon was not found due to coalescence of two signals.

Catalytic activity of titanium complexes in Abramov reaction

Diethyl (*S*)-hydroxy(phenyl)methylphosphonate ((*S*)-(−)-32)

Method 1. At 0 °C benzaldehyde (0.25 g, 2.4 mmol) and diethyl phosphite (0.46 g, 2.9 mmol) were added dropwise to a solution of complex **20** (0.09 g, 0.2 mmol, 10 mol%) in toluene (5 mL) and the reaction mixture was stirred for 20 h. The mixture was then treated with saturated aqueous $NaHCO_3$ and extracted with ether or dichloromethane. The combined

extracts were washed with brine, dried (Na_2SO_4) and concentrated. Purification of the residue by flash chromatography (SiO_2, hexane–EtOAc, 2 : 1) gave (*S*)-(−)-**32** (0.49 g, 84%) as a white solid; $[\alpha]_D^{22}$ −7.8 (*c* 1.0 in $CHCl_3$) for a sample of 24% ee; δ_H (400.1 MHz, $CDCl_3$, ppm) 7.49–7.44 (2H, m, CH_{arom}), 7.37–7.26 (3H, m, CH_{arom}), 5.00 (1H, dd, *J* 11.0 and 4.9, OCH), 3.46 (1H, br s, OH), 4.09–3.92 (4H, m, $2OCH_2CH_3$), 1.25, 1.19 (each 3H, each t, *J* 7.1, $2CH_2CH_3$); δ_P (160 MHz, $CDCl_3$, ppm) 21.15; spectral data were identical with those reported in literature.[19a]

Method 2. Analogously to the above procedure compound (*S*)-(−)-**32** (0.45 g, 83%) was prepared from benzaldehyde (0.24 g, 2.3 mmol), diethyl phosphite (0.37 g, 2.7 mmol) and complex **22** (0.10 g, 0.2 mmol, 10 mol%) in THF (4 mL); $[\alpha]_D^{22}$ −12.4 (*c* 1.0 in $CHCl_3$) for a sample of 38% ee.

Method 3. Analogously to the above procedure compound (*S*)-(−)-**32** (0.44 g, 78%) was prepared from benzaldehyde (0.24 g, 2.3 mmol), diethyl phosphite (0.37 g, 2.7 mmol) and complex **26** (0.15 g, 0.2 mmol, 10 mol%) in toluene (5 mL); $[\alpha]_D^{22}$ −6.8 (*c* 1.0 in $CHCl_3$) for a sample of 20% ee.

Method 4. Analogously to the above procedure compound (*S*)-(−)-**32** (0.40 g, 74%) was prepared from benzaldehyde (0.23 g, 2.2 mmol), diethyl phosphite (0.36 g, 2.6 mmol) and complex **28** (0.16 g, 0.2 mmol, 10 mol%) in THF (4 mL); $[\alpha]_D^{22}$ −2.3 (*c* 1.0 in $CHCl_3$) for a sample of 10% ee.

Diethyl (*R*)-hydroxy(phenyl)methylphosphonate ((*R*)-(+)-32)

Method 1. Analogously to (*S*)-(−)-**32**, compound (*R*)-(+)-**32** (0.44 g, 81%) was prepared from benzaldehyde (0.24 g, 2.2 mmol), diethyl phosphite (0.37 g, 2.7 mmol) and complex **23** (0.11 g, 0.2 mmol, 10 mol%) in THF (4 mL); $[\alpha]_D^{22}$ +8.5 (*c* 1.0 in $CHCl_3$) for a sample of 24% ee; other physical data were identical with those of (*S*)-(−)-**32**

Method 2. Analogously to the above procedure with using benzaldehyde (0.25 g, 2.4 mmol), diethyl phosphite (0.46 g, 2.9 mmol) and **25** (0.14 g, 0.3 mmol, 11 mol%) in THF (4 mL) gave (*R*)-(+)-**32** (0.48 g, 82%); $[\alpha]_D^{22}$ +10.8 (*c* 1.0 in $CHCl_3$) for a sample of 30% ee.

Method 3. Analogously to the above procedure with using benzaldehyde (0.24 g, 2.2 mmol), diethyl phosphite (0.37 g, 2.7 mmol) and **30** (0.15 g, 0.2 mmol, 10 mol%) in THF (4 mL) gave (*R*)-(+)-**32** (0.42 g, 78%); $[\alpha]_D^{22}$ +8.8 (*c* 1.0 in $CHCl_3$) for a sample of 28% ee.

Diethyl (*S*)-hydroxy(3-nitrophenyl)methylphosphonate ((*S*)-(−)-33). Analogously to (*S*)-(−)-**32**, compound (*S*)-(−)-**33** (0.47 g, 74%) was prepared from 3-nitrobenzaldehyde (0.33 g, 2.2 mmol), diethyl phosphite (0.37 g, 2.7 mmol) and complex **22** (0.10 g, 0.2 mmol, 10 mol%) in toluene (5 mL); $[\alpha]_D^{22}$ −11.2 (*c* 1.0 in $CHCl_3$) for a sample of 28% ee; δ_H (400.1 MHz, $CDCl_3$, ppm) 8.39–8.35, 8.18–8.13, 7.82–7.78, 7.56–7.49 (each 1H, each m, CH_{arom}), 5.14 (1H, dd, *J* 10.8 and 4.5, OCH), 4.16–4.06 (4H, m, $2OCH_2CH_3$), 3.62 (1H, br s, OH), 1.31–1.22 (6H, m, $2CH_2CH_3$); spectral data were identical with those reported in literature.[28]

Diethyl (*R*)-hydroxy(3-nitrophenyl)methylphosphonate ((*R*)-(+)-33). Analogously to (*S*)-(−)-**32**, compound (*R*)-(+)-**33** (0.46 g, 72%) was prepared from 3-nitrobenzaldehyde (0.33 g, 2.2 mmol), diethyl phosphite (0.37 g, 2.7 mmol) and complex **30** (0.13 g, 0.2 mmol, 10 mol%) in THF (4 mL); $[\alpha]_D^{22}$ +3.4 (*c* 1.0 in $CHCl_3$) for a sample of 10% ee; other physical data were identical with those of (*S*)-(−)-**33**.

Diethyl (*S*)-hydroxy(4-methoxyphenyl)methylphosphonate ((*S*)-(−)-34). Analogously to (*S*)-(−)-**32**, compound (*S*)-(−)-**34** (0.49 g, 81%) was prepared from 4-methoxybenzaldehyde (0.30 g, 2.2 mmol), diethyl phosphite (0.37 g, 2.7 mmol) and complex **22** (0.10 g, 0.2 mmol, 10 mol%) in toluene (5 mL); $[\alpha]_D^{22}$ −12.3 (*c* 1.0 in $CHCl_3$) for a sample of 34% ee; δ_H (400.1 MHz, $CDCl_3$, ppm) 7.41–7.37 (2H, m, CH_{arom}), 6.88 (2H, d, *J* 8.6, CH_{arom}), 4.93 (1H, dd, *J* 10.1 and 4.8, OCH), 4.09–3.91 (4H, m, $2OCH_2CH_3$), 3.21 (1H, br s, OH), 1.26, 1.20 (each 3H, each t, *J* 7.1, $2CH_2CH_3$); spectral data were identical with those reported in literature.[19a]

Diethyl (*R*)-hydroxy(4-methoxyphenyl)methylphosphonate ((*R*)-(+)-34). Analogously to (*S*)-(−)-**32**, compound (*R*)-(+)-**34** (0.34 g, 56%) was prepared from 4-methoxybenzaldehyde (0.30 g, 2.2 mmol), diethyl phosphite (0.37 g, 2.7 mmol) and complex **30** (0.15 g, 0.2 mmol, 10 mol%) in THF (4 mL); $[\alpha]_D^{22}$ +4.8 (*c* 1.0 in $CHCl_3$) for a sample of 12% ee; other physical data were identical with those of (*S*)-(−)-**34**.

Dimethyl (*S*)-hydroxy(phenyl)methylphosphonate ((*S*)-(−)-35). Analogously to (*S*)-(−)-**32**, compound (*S*)-(−)-**35** (0.35 g, 73%) was prepared from benzaldehyde (0.23 g, 2.2 mmol), dimethyl phosphite (0.31 g, 2.9 mmol) and complex **22** (0.10 g, 0.2 mmol, 10 mol%) in toluene (5 mL); $[\alpha]_D^{22}$ −4.0 (*c* 1.0 in EtOH) for a sample of 16% ee; δ_H (400.1 MHz, $CDCl_3$, ppm) 7.49–7.43 (2H, m, CH_{arom}), 7.38–7.28 (3H, m, CH_{arom}), 5.04 (1H, dd, *J* 10.9 and 5.3, OCH), 3.80–3.76 (1H, m, OH), 3.69, 3.65 (each 3H, each d, *J* 10.4, $2OCH_3$); δ_P (160 MHz, $CDCl_3$, ppm) 19.79; spectral data were identical with those reported in literature.[29]

Diisopropyl (*S*)-hydroxy(phenyl)methylphosphonate ((*S*)-(−)-36)

Method 1. Analogously to (*S*)-(−)-**32**, compound (*S*)-(−)-**36** (0.48 g, 81%) was prepared from benzaldehyde (0.23 g, 2.2 mmol), diisopropyl phosphite (0.47 g, 2.8 mmol) and complex **22** (0.10 g, 0.2 mmol, 10 mol%) in toluene (5 mL); mp 93–94 °C; $[\alpha]_D^{22}$ −14.1 (*c* 1.3 in Me_2CO) for a sample of 50% ee; δ_H (400.1 MHz, $CDCl_3$, ppm) 7.49–7.43 (2H, m, CH_{arom}), 7.35–7.25 (3H, m, CH_{arom}), 4.94 (1H, dd, *J* 11.0 and 5.0, OCHP), 4.66–4.53 (2H, m, 2OCH), 3.52–3.44 (1H, m, OH), 1.27–1.21 (9H, m, $3CHCH_3$), 1.11 (3H, d, *J* 6.1, $CHCH_3$); δ_P (160 MHz, $CDCl_3$, ppm) 23.45; spectral data were identical with those reported in literature.[29b] .

Method 2. Analogously to (*S*)-(−)-**32**, compound (*S*)-(−)-**36** (0.46 g, 73%) was prepared from benzaldehyde (0.27 g, 2.6 mmol), diisopropyl phosphite (0.56 g, 3.4 mmol) and complex **29** (0.16 g, 0.2 mmol, 12 mol%) in toluene (5 mL); mp 96–97 °C; $[\alpha]_D^{22}$ −13.0 (*c* 1.3 in Me_2CO) for a sample of 46% ee.

Diisopropyl (*S*)-(2-bromophenyl)(hydroxy)methylphosphonate ((*S*)-(−)-37). Analogously to (*S*)-(−)-**32**, compound (*S*)-(−)-**37** (0.65 g, 84%) was prepared from 2-bromobenzaldehyde (0.41 g, 2.2 mmol), diisopropyl phosphite (0.58 g, 3.5 mmol) and complex **22** (0.10 g, 0.2 mmol, 10 mol%) in toluene (5 mL); mp 83–84 °C; $[\alpha]_D^{22}$ −8.7 (*c* 1.5 in $CHCl_3$) for a sample of 14% ee; δ_H (400.1 MHz, $CDCl_3$, ppm) 7.75–7.71, 7.53–7.49, 7.35–7.30, 7.17–7.10 (each 1H, each m, CH_{arom}), 5.44 (1H, dd, *J* 12.4 and 6.4, OCHP), 4.78–4.67, 4.63–4.52 (each 1H, each m, 2OCH), 4.17–4.11 (1H, m, OH), 1.34, 1.28, 1.24, 1.06 (each 3H, each d, *J* 6.2, $CHCH_3$); δ_P (160 MHz, $CDCl_3$, ppm) 19.52; spectral data were identical with those reported in literature.[30]

Diisopropyl (*S*)-hydroxy(4-methoxyphenyl)methylphosphonate ((*S*)-(−)-38). Analogously to (*S*)-(−)-**32**, compound (*S*)-(−)-**38** (0.45 g, 68%) was prepared from 4-methoxybenzaldehyde (0.30 g, 2.2 mmol), diisopropyl phosphite (0.58 g, 3.5 mmol) and complex **22** (0.10 g, 0.2 mmol, 10 mol%) in toluene (5 mL); mp 150 °C; $[\alpha]_D^{22}$ −7.5 (*c* 0.8 in $CHCl_3$) for a sample of 35% ee; δ_H (400.1 MHz, $CDCl_3$, ppm) 7.39 (2H, dd, *J* 8.6 and 2.0, CH_{arom}), 6.87 (2H, d, *J* 8.6, CH_{arom}), 4.86 (1H, dd, *J* 10.1 and 4.8, OCHP), 4.66–4.54 (2H, m, 2OCH), 3.79 (3H, s, OCH_3), 2.74–2.69 (1H, m, OH), 1.29–1.22 (9H, m, $3CHCH_3$), 1.12 (3H, d, *J* 6.3, $CHCH_3$); δ_P (160 MHz, $CDCl_3$, ppm) 19.96; spectral data were identical with those reported in literature.[30]

Diisopropyl (*S*)-hydroxy(3-nitrophenyl)methylphosphonate ((*S*)-(−)-39). Analogously to (*S*)-(−)-**32**, compound (*S*)-(−)-**39** (0.53 g, 76%) was prepared from 3-nitrobenzaldehyde (0.33 g, 2.2 mmol), diisopropyl phosphite (0.47 g, 2.8 mmol) and complex **22** (0.10 g, 0.2 mmol, 10 mol%) in toluene (5 mL); mp 103–105 °C; $[\alpha]_D^{22}$ −30.0 (*c* 0.13 in $CHCl_3$) for a sample of 52% ee; $C_{13}H_{20}NO_6P$ requires C, 49.2; H, 6.35%; found C, 49.1; H, 6.3%; δ_H (400.1 MHz, $CDCl_3$, ppm) 8.39–8.35, 8.17–8.11, 7.83–7.78, 7.53–7.48 (each 1H, each m, CH_{arom}), 5.08 (1H, dd, *J* 11.3 and 5.1, OCHP), 4.77–4.58 (2H, m, 2OCH), 5.63 (1H, br s, OH), 1.30–1.24 (9H, m, $3CHCH_3$), 1.22 (3H, d, *J* 6.3, $CHCH_3$); δ_P (160 MHz, $CDCl_3$, ppm) 18.18; δ_C (100.61 MHz, $CDCl_3$, 50 °C, ppm) 147.99 (s), 139.55 (d, J_{PC} 2.3), 133.13 (d, J_{PC} 5.1), 128.74 (d, J_{PC} 2.9), 122.55 (d, J_{PC} 2.9), 122.17 (d, J_{PC} 5.1) (C_{arom} and CH_{arom}), 72.73 (d, J_{PC} 7.3), 72.13 (d, J_{PC} 8.1 ГII) ($2OCHMe_2$), 69.97 (d, J_{PC} 161.0, OCHP), 24.09 (d, J_{PC} 2.9), 23.92 (d, J_{PC} 5.9), 23.86 (d, J_{PC} 3.7), 23.60 (d, J_{PC} 5.1) ($4OCH(CH_3)_2$).

Diisopropyl (*S*)-(4-fluorophenyl)(hydroxy)methylphosphonate ((*S*)-(−)-40). Analogously to (*S*)-(−)-**32**, compound (*S*)-(−)-**40** (0.53 g, 76%) was prepared from 4-fluorobenzaldehyde (0.22 g, 1.8 mmol), diisopropyl phosphite (0.47 g, 2.8 mmol) and complex **22** (0.10 g, 0.2 mmol, 10 mol%) in toluene (5 mL); mp 92–93 °C; $[\alpha]_D^{22}$ −80.0 (*c* 0.1 in $CHCl_3$) for a sample of 40% ee; $C_{13}H_{20}FO_4P$ requires C, 53.8; H, 6.9%; found C, 53.4; H, 6.8%; δ_H (400.1 MHz, $CDCl_3$, ppm) 7.47–7.41, 7.05–6.98 (each 2H. each m, CH_{arom}), 4.91 (1H, dd, *J* 10.4 and 3.0, OCHP), 4.67–4.55 (2H, m, OCH), 3.70 (1H, br s, OH), 1.27–1.21 (9H, m, $3CHCH_3$), 1.14 (3H, d, *J* 6.2, $CHCH_3$); δ_P (160 MHz, $CDCl_3$, ppm) 19.43 (d, J_{FP} 3.3); δ_C (100.61 MHz, $CDCl_3$, ppm) 162.47 (dd, J_{FC} 245.9, J_{PC} 2.9, C_5H_4CF), 132.46 (s, C_5H_4CCH), 128.88 (dd, J_{FC} 8.1, J_{PC} 5.9, *m*-C_6H_4F), 115.00 (dd, J_{PC} 21.7, J_{FC} 2.2, *o*-C_6H_4F), 72.02, 71.74 (each d, J_{PC} 7.4, $2OCHMe_2$), 70.39 (d, J_{PC} 161.0, *C*H(OH)), 24.12, 24.01 (each d, J_{PC} 3.7, $OCH(CH_3)_2$), 23.86, 23.61 (each d, J_{PC} 5.1, $OCH(CH_3)_2$).

Diisopropyl (*S*)-hydroxy(thien-2-yl)methylphosphonate ((*S*)-(−)-41). Analogously to (*S*)-(−)-**32**, compound (*S*)-(−)-**41** (0.41 g, 68%) was prepared from thiophene-2-carbaldehyde (0.25 g, 2.2 mmol), diisopropyl phosphite (0.58 g, 3.5 mmol) and complex **22** (0.10 g, 0.2 mmol, 10 mol%) in toluene (5 mL); mp 73–74 °C; $[\alpha]_D^{22}$ −24.0 (*c* 0.17 in $CHCl_3$) for a sample of 56% ee; $C_{11}H_{19}O_4PS$ requires C, 47.5; H, 6.9%; found C, 47.4; H, 6.8%; δ_H (400.1 MHz, $CDCl_3$, ppm) 7.28–7.24, 7.17–7.14, 6.98–6.94 (each 1H, each m, thiophene), 5.13 (1H, dd, *J* 11.0 and 5.1, OCHP), 4.74–4.62 (2H, m, OCH), 4.38 (1H, br s, OH), 1.29 (3H, d, *J* 6.2, $CHCH_3$), 1.24 (6H, d, *J* 6.2, $2CHCH_3$), 1.17 (3H, d, *J* 6.2, $CHCH_3$); δ_P (160 MHz, $CDCl_3$, ppm) 18.03; δ_C (100.61 MHz, $CDCl_3$, ppm) 140.09 (s), 126.56 (s), 126.02 (d, J_{PC} 7.3), 125.34 (d, J_{PC} 2.9) (thiophene), 72.24 (d, J_{PC} 6.6, $OCHMe_2$), 71.94 (d, J_{PC} 7.3, $OCHMe_2$), 67.42 (d, J_{PC} 168.3, OCHP), 24.10 (d, J_{PC} 2.9), 23.98 (d, J_{PC} 3.7), 23.81 (d, J_{PC} 4.4), 23.56 (d, J_{PC} 5.1) ($4OCH(CH_3)_2$).

General procedure for determination of absolute configuration of hydroxy(aryl)methyl phosphonates 39–41. To a stirred solution of corresponding hydroxy(aryl)methyl phosphonate **39–41** (0.36 mmol), *O*-acetyl-(*S*)-(+)-mandelic acid **8** (0.091 g, 0.47 mmol) and 4-dimethylaminopyridine (DMAP) (0.004 g, 0.036 mmol) in CH_2Cl_2 (3 mL) was added a solution of *N*,*N*-dicyclohexylcarbodiimide (DCC) (0.097 g, 0.47 mmol) in CH_2Cl_2 (2 mL) at 0 °C.[13a,21a] The mixture was stirred at the same temperature for 30 min and then kept at room temperature until the starting material had disappeared as evidenced by TLC (20–22 h). The solution was filtered and diluted with water (5 mL) after which it was extracted with CH_2Cl_2. The extracts were washed with saturated aqueous $NaHCO_3$, water, dried (Na_2SO_4) and then concentrated *in vacuo*. The residue was analysed by NMR spectroscopy ($CDCl_3$) without purification. ^1H (for AcOC*H* group) and ^{31}P NMR data of these samples are listed in Table 5.

X-Ray crystallography

Experimental data were collected at 120 K on Bruker SMART 1K diffractometer (for **23**, **25**, **28**, **31**) and on Bruker SMART APEX diffractometer (for **26**, **27**, **30**) using Mo-Kα radiation (λ = 0.71073 Å). Absorption corrections based on measurements of equivalent reflections were applied. The structures were solved by direct methods[31] and refined by full-matrix least squares based on F^2 with anisotropic thermal parameters for all non-hydrogen atoms.[32] In the structures **26** all hydrogen atoms were found from difference Fourier synthesis and refined isotropically; in **23**, **25**, **27**, **28**, **30** and **31** all hydrogen atoms were placed in calculated positions and refined using a riding model. Crystal data, data collection and refinement parameters are given in Table 7.

CCDC reference numbers 679771, 679772 and 683792–683796.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b714739b

Table 7 Crystal data, data collection and refinement parameters for complexes **23**, **25–28**, **30** and **31**

Compound	**23**	**25**	**26**	**27**	**28**	**30**	**31**
Empirical formula	$C_{27}H_{39}NO_4Ti$	$C_{32}H_{50}N_2O_4Ti$	$C_{40}H_{50}N_2O_4Ti$	$C_{28}H_{42}N_2O_4Ti\cdots CH_2Cl_2$	$C_{48}H_{50}N_2O_4Ti$	$C_{42}H_{50}N_2O_4Ti$	$C_{62}H_{58}N_2O_4Ti\cdots CH_2Cl_2$
M	489.49	574.64	670.72	603.46	766.80	694.74	1027.93
Crystal size/mm	0.20 × 0.20 × 0.15	0.10 × 0.10 × 0.06	0.35 × 0.2 × 0.20	0.25 × 0.20 × 0.16	0.20 × 0.20 × 0.16	0.25 × 0.20 × 0.18	0.20 × 0.16 × 0.14
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$	$C222_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a/Å	10.8754(8)	8.6073(4)	10.8805(14)	10.162(3)	11.3503(12)	11.096(2)	11.9885(5)
b/Å	14.0332(11)	18.8704(9)	17.269(2)	10.972(3)	17.9768(19)	12.761(2)	19.3301(9)
c/Å	17.5810(14)	19.0174(9)	18.868(3)	27.065(8)	20.083(2)	26.595(5)	22.2363(10)
V/Å^3	2683.2(4)	3088.9(3)	3545.3(8)	3017.6(16)	4097.8(7)	3766.0(12)	5153.0(4)
Z	4	4	4	4	4	4	4
D_c/Mg m^{-3}	1.212	1.236	1.257	1.328	1.243	1.225	1.325
μ/mm^{-1}	0.350	0.314	0.284	0.497	0.255	0.270	0.322
$F(000)$	1048	1240	1432	1280	1624	1480	2160
θ Range/°	1.86–28.00	1.52–27.00	3.09–28.00	2.39–27.99	1.52–27.00	2.43–27.99	1.40–29.50
Reflections collected	17 527	19 614	13 938	21 553	25 710	24 191	38 038
Independent reflections	6473	6735	4121	7219	8944	9038	14 137
R_{int}	0.0594	0.0879	0.0505	0.0362	0.0925	0.0502	0.0682
Data/restraints/param.	6473/0/304	6735/0/362	4121/0/313	7219/0/351	8944/0/500	9038/0/446	14137/0/649
R indices [$I > 2\sigma(I)$]	R_1 = 0.0552, wR_2 = 0.0875	R_1 = 0.0590, wR_2 = 0.0957	R_1 = 0.0444, wR_2 = 0.0898	R_1 = 0.0453, wR_2 = 0.1201	R_1 = 0.0627, wR_2 = 0.1006	R_1 = 0.0514, wR_2 = 0.1018	R_1 = 0.0544, wR_2 = 0.0924
R indices (all data)	R_1 = 0.0877, wR_2 = 0.0953	R_1 = 0.0898, wR_2 = 0.1029	R_1 = 0.0557, wR_2 = 0.0937	R_1 = 0.0508, wR_2 = 0.1234	R_1 = 0.1006, wR_2 = 0.1098	R_1 = 0.0638, wR_2 = 0.1058	R_1 = 0.0896, wR_2 = 0.1008
GOF on F^2	1.037	1.014	1.045	1.060	1.004	1.018	1.015
Flack parameter	−0.02(3)	0.02(3)	0.01(3)	0.00(2)	−0.01(3)	0.00(2)	0.02(2)
Largest diff. peak, hole/e A^{-3}	0.329, −0.449	0.376, −0.356	0.324, −0.627	0.512, −0.716	0.332, −0.358	0.472, −0.922	0.273, −0.464

Conclusions

In conclusion, we have synthesized a series of chiral dialkanolamines and the corresponding titanocanes and spirobititanocanes on the basis of these compounds. The characteristic structural features of titanium derivatives were established in solution and in the solid state. The Ti complexes obtained were used as enantioselective catalysts in the Abramov reaction. We expect that these results will be synthetically and structurally useful for further investigations in organic and organometallic chemistry and in chiral catalysis.

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