146. Polymer- and Dendrimer-Bound Ti-TADDOLates in Catalytic (and Stoichiometric) Enantioselective Reactions: Are Pentacoordinate Cationic Ti Complexes the Catalytically Active Species?

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α,α,α′,α′-*T*etra*a*ryl-1,3-*d*ioxolane-4,5-*d*imethan*o*l*s* (TADDOLs), containing styryl groups either at C(2) of the heterocyclic ring or in the α-position, were prepared in the usual way (**18**–**22**, **24**, **25**). These compounds were copolymerized with styrene and divinylbenzene in a suspension, yielding polymers (**33**–**40**, *Scheme 3*) as beads with a rather uniform particle-size distribution (150–450 μm), swellable in common organic solvents. $HOCH_2$- and $BrCH_2$-substituted TADDOLs were also prepared and used for attachement to *Merrifield* resin or to dendritic molecules (**23**, **26**–**32**). The TADDOL moieties in these materials are accessible to form Ti (and Al) complexes (*Scheme 4*) which can be used as polymer- or dendrimer-bound reagents (stoichiometric) or *Lewis* acids (catalytic). The reactions studied with these new chiral auxiliaries are: enantioselective nucleophilic additions to aldehydes (of R_2Zn and $RTi(OCHMe_2)_3$; *Scheme 5*, *Table 1*) and to ketones (of $LiAlH_4$, *Table 2*); enantioselective ring opening of *meso*-anhydrides (*Scheme* 6); [4+2] and [3+2] cycloadditions of 3-crotonyl-1,3-oxazolidin-2-one to cyclopentadiene and to (*Z*)-*N*-benzylidenephenylamine *N*-oxide (→ **48**, **49**, *Scheme 7*, *Tables 3*, *4*, and *Fig. 5*). The enantioselectivities reached with most of the polymer-bound or dendritic TADDOL ligands were comparable or identical to those observed with the soluble analogs. The activity of the polymer-bound *Lewis* acids was only slightly reduced as compared with that encountered under homogeneous conditions. Multiple use of the beads (up to 10 times), without decreased performance, has been demonstrated (*Figs. 3* and *4*). The poorer selectivity in the *Diels-Alder* reaction (*Scheme 7a*), induced by the polymer-bound Cl_2Ti-TADDOLate as compared to the soluble one, is taken as an opportunity to discuss the mechanism of this *Lewis*-acid catalysis, and to propose a cationic, trigonal-bipyramidal complex as the catalytically active species (*Fig. 6*). It is suggested that similar cations may be involved in other Ti-TADDOLate-mediated reactions as well.

1. Introduction. – TADDOLs (= α,α,α′,α′-tetraaryl-1,3-dioxolane-4,5-dimethanols), the products from tartrate acetals and aryl *Grignard* reagents [1] (*cf.* **1**–**5** in *Scheme 1*), have found many applications in EPC synthesis [3]: as chiral ligands for metal centers, in stoichiometric and catalytic enantioselective reactions, and as H-bonding compounds (*cf.* clathrate formation). The variety of different reactions which can be rendered enantioselective is even increased by using TADDOL derivatives modified in such a way that they contain N-, P-, and S-atoms for complexation (see review articles [1] [4–7]). Usually, products are separated from TADDOLs by aqueous extraction, by distillation, or by chromatography; in the latter two cases, this may be tedious, especially due to the clathrating properties of these diols[3]). We have, therefore, set off to prepare polymer-bound TADDOLs with which these complications could be avoided. This is, of course,

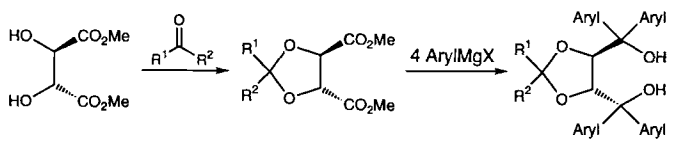
[1]) Part of the Dissertation No. 11571 of *R. E. M.*, ETH Zürich, 1996.

[2]) Part of the Master Thesis of *T. H.*, ETH Zürich, 1995

[3]) For a case in which this property could be exploited for obtaining better results, see [7] [8].

by no means a new idea: numerous catalysts and reagents have been modified by attaching them to solid phases[4]), and syntheses on solid support, first reported by *Merrifield* [10], and *Letsinger* and *Kornet* [11], are now part of standard methodology, having experienced a boost, recently, by the introduction of combinatorial synthesis [12]. To the best of our knowledge, there is only one report about unsuccessful experiments towards attaching a TADDOL unit to a polymer [13], and polymerizable TADDOL derivatives (methacrylate esters) have only been described in one instance [14].

Scheme 1. *Preparation of TADDOLs from Tartrate and Aryl* Grignard *Reagents.* The five examples shown here are the TADDOLs to be compared with polymer-bound analogs in this paper; for a complete list as of October 1994, see [2].



TADDOLs

	R^1	R^2	Aryl
1	Me	Me	Ph
2	Me	Me	1-Naphthyl
3	Me	Me	2-Naphthyl
4	Ph	Ph	Ph
5	H	Ph	Ph

2. Preparation of TADDOLs Which Can Be Attached to *Merrifield* Resin, Which Can Be Linked with Dendritic Molecules, or Which Are Polymerizable. – We chose to study two sites of attachement of TADDOL units to polymers: *i*) the *para*-position of a benzene ring on the dioxolane-acetal center and *ii*) the *para*-position of benzene rings at the diarylmethanol moiety. To this end, we prepared the TADDOLs **18**–**26**, starting materials being the aldehyde **6** and the ketones **7**, **8** (all known compounds[5])), as well as the acetals **9**, **10**, **14**, and **15**, from which we obtained the dimethyl-tartrate-derived dioxolanes **11**–**13** and **16**. Another starting material was the hydroxy ester **17**, previously described by us [15].

The esters **11**–**13**, **16**, and **17** were then allowed to react with 4–5 equiv. of aryl *Grignard* reagents[6]) to give the TADDOLs **18**–**24**. The reactions leading to TADDOLs containing styryl groups have to be carried out under somewhat milder conditions (no heating in the *Grignard* addition step), in order to prevent the formation of polymeric materials or side products, which are difficult to separate. Otherwise, the new vinyl TADDOLs have very similar properties to those observed with ordinary analogs (*cf. Scheme 1*). The $HOCH_2$-substituted TADDOL **23** was used for the preparation of a styryl-containing derivative **25** in which there is a spacer between the TADDOL unit and the backbone of the polymer to be formed; **23** was also used as the precursor to the acrylate ester **26**.

Finally, the triol **23** and the corresponding bromo derivative **27** were the starting materials for the preparation of dendritic molecules **28**–**30** (zero generation) and **31** (1st generation) containing terminal TADDOL moieties at the branches: the commercially available benzene-1,3,5-tricarbonyl trichloride was coupled with **23** to give the hexahydroxytriester **28**, and a tris(acid chloride)[7]), obtained from benzene-1,3,5-tricarboxylic

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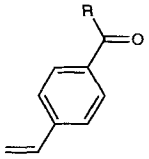
[4]) For books and reviews covering all aspects of this area, see *e.g.* [9].

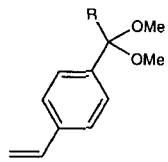
[5]) For references, see *Exper. Part.*

[6]) For the reaction **16** → **23**, a larger excess of PhMgBr is necessary due to the presence of the benzoate group.

[7]) This acid chloride was prepared in the course of our work on dendrimers [16].



6-8



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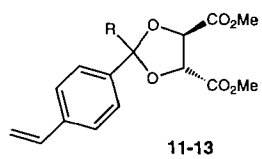
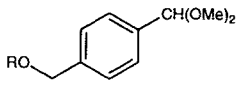


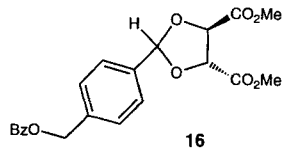
11-13

	6	7	8	9	10
R	H	Me	Ph	Me	Ph

	11	12	13
R	H	Me	Ph



14 R = H
15 R = PhCO (= Bz)



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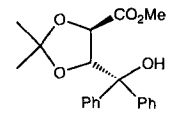

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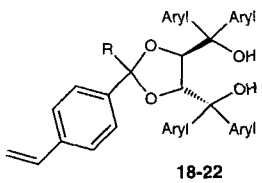
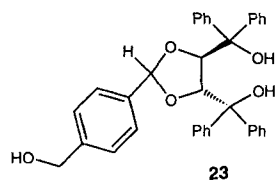
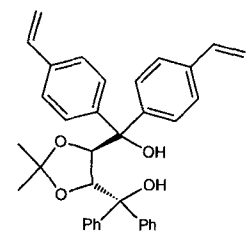


18-22

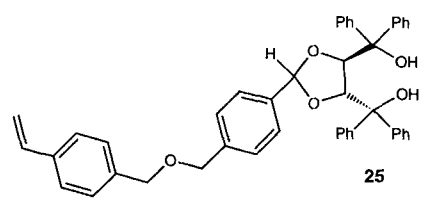


23

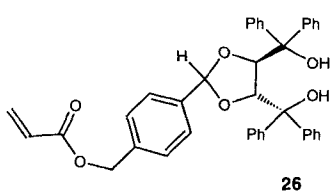


24

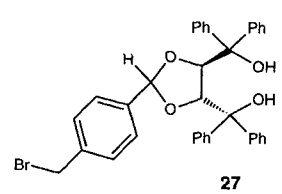
	18	19	20	21	22
R	H	H	H	Me	Ph
Aryl	Ph	1-Naphthyl	2-Naphthyl	Ph	Ph



25

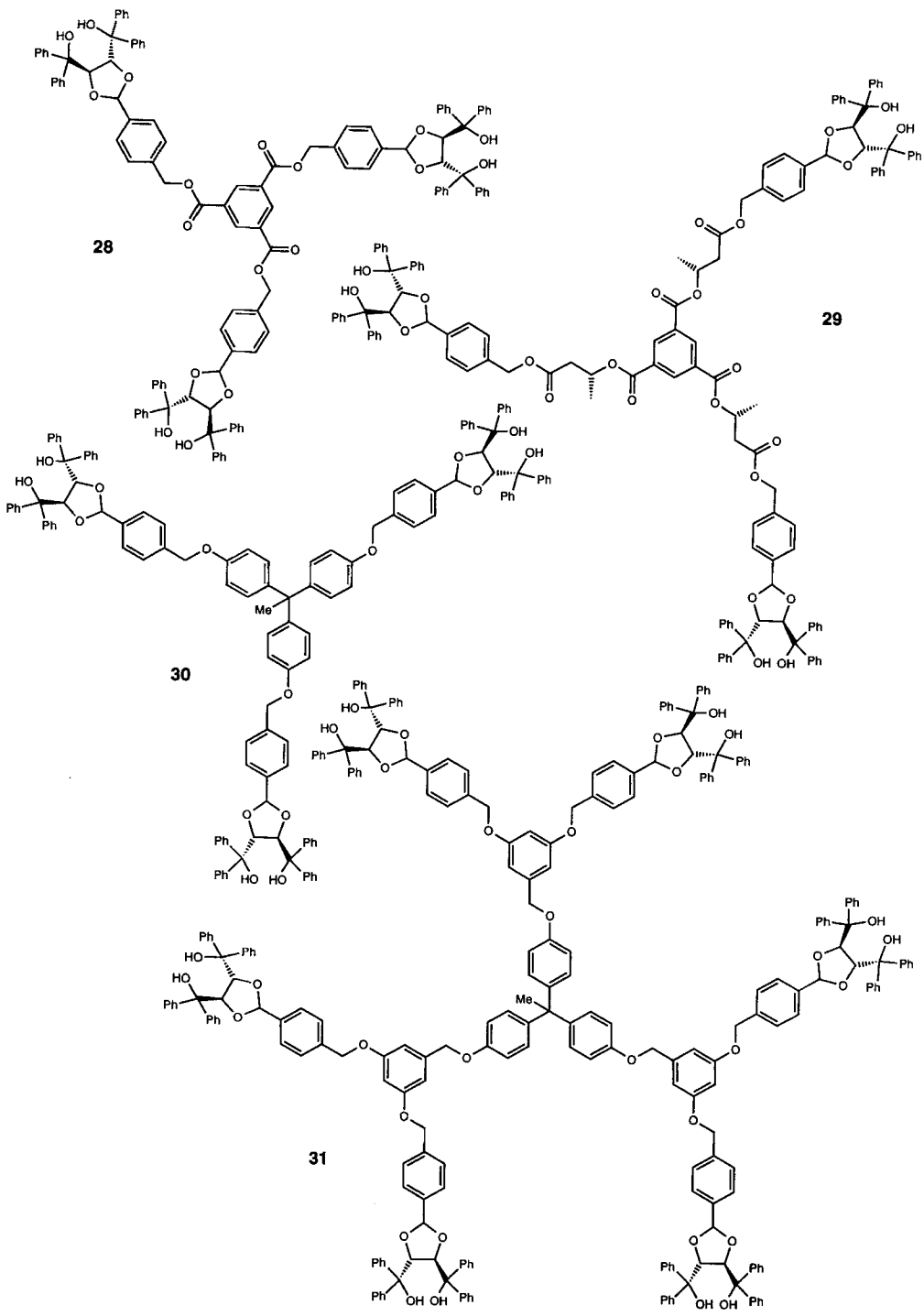


26



27

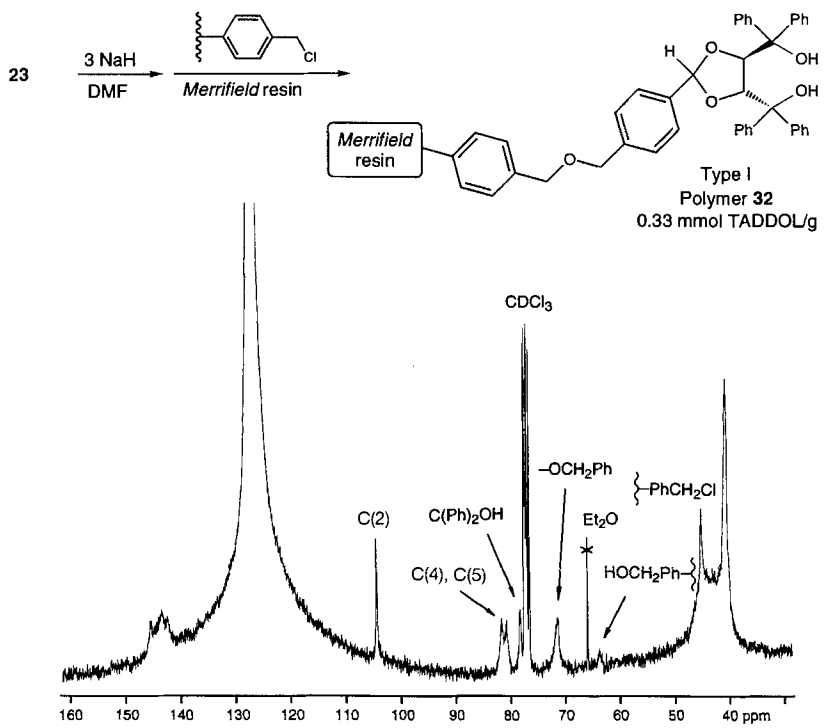
acid and (*R*)-3-hydroxybutanoic acid, gave the zero-generation dendritic compound **29**. For etherifying coupling reactions, we converted the benzylic alcohol **23** to the bromo derivative **27** (CBr_4/PPh_3 in THF) which was used to combine three TADDOL-containing molecules through the commercially available 1,1,1-tris(4-hydroxyphenyl)ethane to give the hexol **30**, another zero-generation dendritic derivative. Double etherification of the 3,5-dihydroxybenzyl alcohol (also commercially available) with **27**, OH/Br exchange in the benzylic position and coupling with the phenolic triol mentioned above gave the 1st-generation dendrimer **31** (mol. weight 3832 D) with six terminal TADDOL units.


28
29
30
31

Knowing about the lability of TADDOL derivatives in which an OH group has been replaced by better leaving groups [15] [17] [18], we are surprised that reactions of the triol **23** with reagents and reactants such as acid chlorides, benzylic bromides, and CBr_4/PPh_3 work neatly (80–90% yields) without protection of the OH groups of the diphenylmethanol units.

3. Suspension Copolymerization of TADDOLs 18–22 and 24–26. – Being no specialists in the field of polymerization, we first prepared a polymer-bound TADDOL from a given polymer (*Scheme 2*). Beads of a typical *Merrifield* resin (2% cross-linking, 0.7 and 1.7 mmol Cl/g) were added to the orange-brown reaction mixture obtained from NaH and **23** in DMF. After 2 d (with slight warming), a modified polymer **32** was obtained by aqueous workup, washing with water, MeOH, and THF, and drying. The TADDOL content was determined gravimetrically to be *ca.* 0.3 mmol/g. The NMR spectrum of the polymer (which we specify as Type I in this paper) is also shown in *Scheme 2*, and the signals characteristic of the TADDOL are clearly visible; the chemical shifts are identical within 0.1 ppm with those of the monomeric analog **25**.

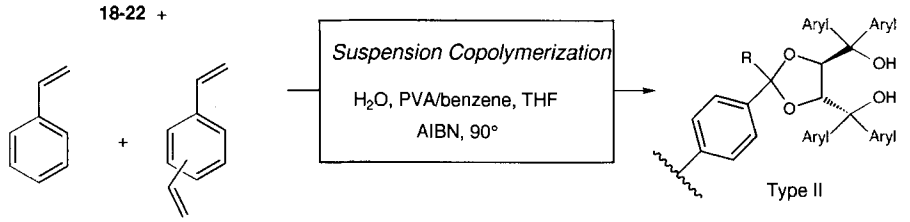
Scheme 2. *Preparation of a TADDOL-Modified* Merrifield *Resin by Etherification of* **23** *with Chloromethylated Polystyrene.* Gel-phase ^{13}C-NMR spectrum (in $CDCl_3$) of the polymer thus obtained.



For the cross-linking radical polymerization, we chose the suspension technique which is known to provide spherical particles of rather uniform sizes, and we followed procedures given in a monograph [19] and in a seminal article by *Fréchet* and coworkers

[20]. Thus, a solution of styrene, divinylbenzene, the styrylic TADDOLs **18–22**, **24**, **25** or the acrylate **26**, and α,α′-azobis[isobutyronitrile] (AIBN) in C_6H_6/THF was mixed with an aqueous phase containing poly(vinyl alcohol) (PVA) and heated (90°/reflux condenser) with constant, slow overhead stirring for two days (see *Exper. Part*).

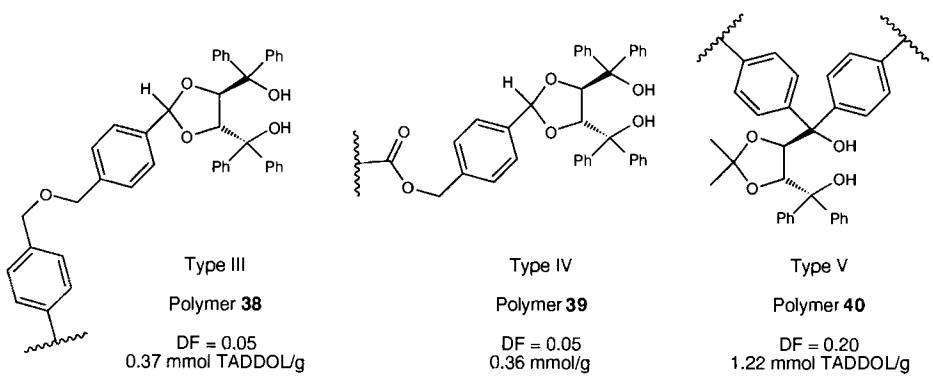
Scheme 3. *Suspension Copolymerization of TADDOL Derivatives* **18–22**, **24**, **25**, *and* **26** *to Give Cross-linked Polymers of Type II–V.* The degrees of functionalization (DF) and loadings (mmol TADDOL/g) are calculated from the relative amounts of the components used in the polymerization.



cross-linked polymers **33-37**

No.	33a	33b	33c	33d	33e	33f	34	35	36	37
R	H	H	H	H	H	H	H	H	Me	Ph
Aryl	Ph	Ph	Ph	Ph	Ph	Ph	1-Naphthyl	2-Naphthyl	Ph	Ph
DF	0.1	0.05	0.025	0.01	0.05[a])	0.05[b])	0.05	0.05	0.05	0.05
mmol/g	0.63	0.36	0.20	0.09	0.40	0.36	0.34	0.36	0.37	0.36

[a]) 10% Cross-linking. [b]) 40% Cross-linking.



This produced quantitatively the polymers of Type II (**33–37**, 'no spacer'), of Type III (**38**, 'with spacer'), of Type IV (**39**, 'polyacrylate'), and of Type V (**40**, 'branching TADDOL')[8]). The beads were isolated by filtering, washing, and drying; their degree of functionalization (DF, molar fraction of TADDOL) and loadings (mmol TADDOL/g)

[8]) Instead of divinylbenzene, we also used tetraethyleneglycol bis(4-vinylbenzyl)ether [21], with the 'parent' TADDOL **18**. The resulting polymer (of Type II) was formed in good yield and with essentially the same physical and mechanical properties as the one obtained by using divinylbenzene; the corresponding Ti complexes were less effective in the reactions tested by us.

are given in *Scheme 3*; the particle size distribution for three of the polymers (**33**, **34**, and **38**) is evident from *Fig. 1*, and a photograph of the sieve fraction 250–400 μm of Type II polymer **34** is shown in *Fig. 2*.

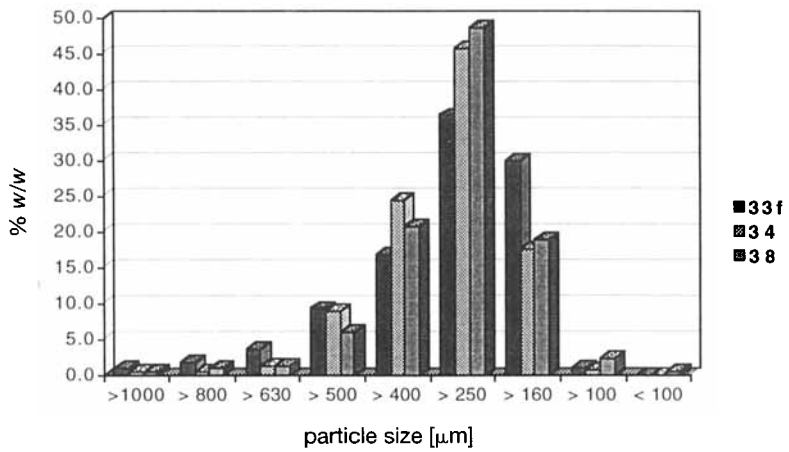


Fig. 1. *Typical particle-size distribution* (in % (*w*/*w*), mesh sizes in μm) *for three different polymers*, **33f**, **34**, *and* **38**, *prepared by suspension copolymerization*

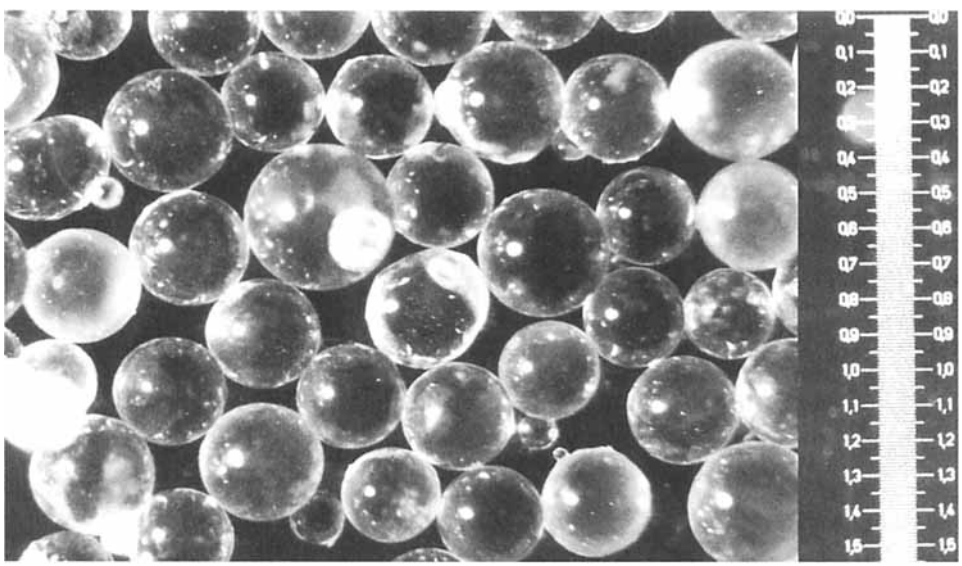


Fig. 2. *Photograph for the transparent beads of Type-II polymer* **34** *obtained by suspension copolymerization* (sieve fraction 250–400 μm, scale in mm)

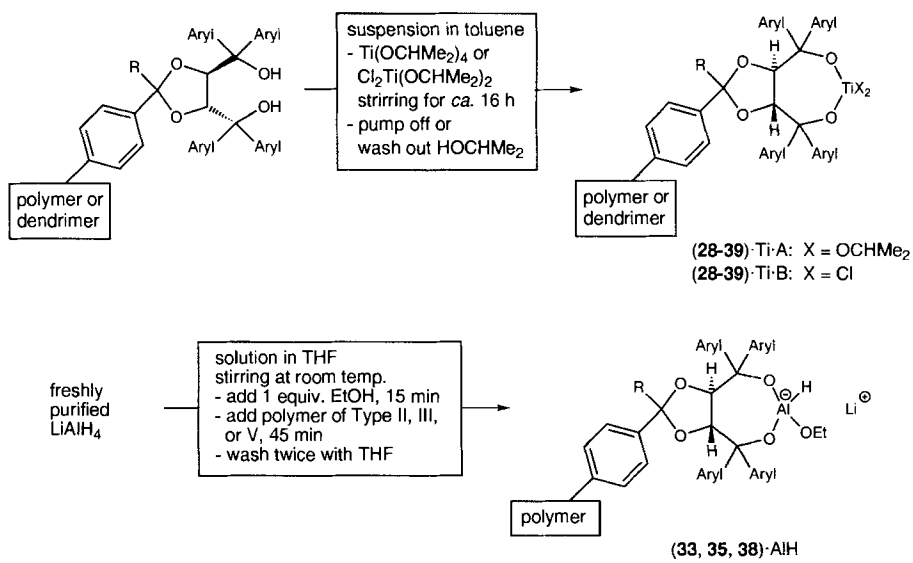
Thus, polymers of reproducible different degrees of functionalization (loadings) and cross-linking could be prepared by suspension copolymerization without any problems[9])

[9]) It is recommended to first test the polymerization apparatus used by a simple copolymerization of styrene and divinylbenzene.

(see *Scheme 3*). The majority (*ca.* 80%) of the beads had a particle size of 0.2–0.5 mm and appeared under a microscope as transparent, 'perfectly formed' spheres. All types (II–V) of polymers prepared by suspension copolymerization swelled in organic solvents such as toluene, THF, Et_2O, CH_2Cl_2, or DMF by a factor of *ca.* 2.5, and in MeOH or pentane by a factor of *ca.* 1.5 in volume.

4. Preparation of Polymer-Bound Ti- and Al-TADDOLates. – For applications of the new polymer-bound TADDOLs, it was crucial that the TADDOL groups are accessible for complexing metal centers, and that the resulting polymer-bound chiral *Lewis*-acid centers are in turn available for reactands to be activated. The procedures used for preparing Ti-TADDOLates from the polymers were pretty much the same as for the homogeneous complexes: as indicated for the polymers of Type I–V in *Scheme 4*, a slurry in toluene was treated with 1.0 equiv. $Ti(OCHMe_2)_4$ or 0.65 equiv. $Cl_2Ti(OCHMe_2)_2$, as calculated for the TADDOL content of the corresponding polymer. After gentle stirring overnight, all volatile components were pumped off (final pressure 0.01 Torr) to give the titanates (**32**–**40**)·Ti·A as slightly yellow beads which were used for mediating the reactions discussed in *Chapt. 5*. For isolating the stronger *Lewis*-acidic dichloro-Ti-TADDOLates (**32**–**40**)·Ti·B, the solvent toluene was decanted by syringe, the orange-yellow Ti-loaded polymer washed thrice with toluene, and used directly. With the dendritic TADDOLs **28**–**31**, a solution in toluene was treated with $Ti(OCHMe_2)_4$ (1.0 equiv.) or with $Cl_2Ti(OCHMe_2)_2$ (0.8 equiv.), leading to formation of a precipitate or of a fine suspension. With the isopropoxy derivatives (**28**–**31**)·Ti·A, the solvent was removed *in vacuo* to give a solid residue which was directly resuspended in the solvent

Scheme 4. *Preparation of Polymer-Bound Ti*-Lewis *Acids and of a Polymer-Bound Hydrido-ethoxy-aluminium-TADDOLate.* The polymer of Type V was converted to Ti- and Al-derivatives **40**·Ti·A, **40**·Ti·B, and **40**·AlH in exactly the same way. For the dendritic Ti-TADDOLates, see accompanying text and *Exper. Part.*



used for subsequent reactions. With the dendritic Cl_2Ti derivatives (**28**–**31**)·Ti·B, the suspension originally formed was employed directly.

To prepare the polymer-bound chiral $LiAlH_4$ derivatives (**33**, **35**, **38**, **40**)·AlH we, again, followed the procedure used for the application under homogeneous conditions [8] (*Scheme 4*), except that, here, we included two washing steps before carrying out the reduction.

We have not analyzed quantitatively the Ti-loaded polymers for their Ti content, but we have no indications that larger amounts of unreacted titanates remained in the supernatent solutions. Also activity tests mentioned in *Chapt. 5* suggest that *ca.* 80% of the calculated TADDOL moieties, and thus of the expected Ti sites, are catalytically active. This would mean that most of the TADDOL groups in the polymers are accessible for titanation, and that most of the Ti-TADDOLates thus formed are active *Lewis*-acidic sites.

5. Applications of Polymer-Bound TADDOLate Complexes for Enantioselective Reactions. – Metal complexes of TADDOLs or TADDOL derivatives have been used either as stoichiometric components of reagents[10]), or they have been employed as *Lewis* acids in equimolar or in excess amounts to mediate reactions[11]), or they have served to catalyze various transformations[12]). We have chosen four representative examples to compare the new polymer-bound TADDOLate complexes with their monomeric counterparts: the nucleophilic alkyl addition to aldehydes, the ring opening of *meso*-anhydrides, [3 + 2] and [4 + 2] cycloadditions, and the complex hydride addition to aryl ketones.

5.1. *R_2Zn and $MeTi(OCHMe_2)_3$ Additions to Aldehydes.* This reaction was thoroughly studied and gives up to and above 99:1 enantioselectivities with various Ti-TADDOLates [41–45]; it is catalytic with respect to the chiral titanate but requires *ca.* 1.2 equiv. of $Ti(OCHMe_2)_4$ for optimal results. We have now employed a stirred mixture containing Ti-TADDOLate beads or the dendrimer-bound Ti-TADDOLate (in an amount corresponding to 0.2 equiv. Ti), 1.2 equiv. $Ti(OCHMe_2)_4$, and 1 equiv. RCHO in toluene, to which 1.8 equiv. Et_2Zn was added at −30° (*Scheme 5, a*). After *ca.* 16 h, 2M aqueous HCl was added, the polymer filtered off and washed with H_2O and Et_2O, and the products **41**, **43**, and **44** were isolated from the organic phases. The yields and enantioselectivities, listed in *Table 1*, are, with one exception, almost identical to those observed with the soluble TADDOLates. Somewhat lower yields and selectivities were observed with the Zn-free reagents $RTi(OCHMe_2)_3$, as compared to the homogeneous conditions (products **42** and **45**, *Scheme 5, b* and *c*, and *Table 1*). The results obtained with the dendritic TADDOLs are also included in *Table 1*; the yields are generally lower, with unchanged selectivities: the ligands **28**–**31** are separated from the poducts by chromatographic

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[10]) For instance, nucleophilic additions of alkyl, allyl, enolate, and hydride to aldehydes [5] [7] [8] [22] [23] and ketones [24], opening of anhydrides [25] and imides [26] by alkoxide, oxidation of TADDOLato-Ti-enolates [27].

[11]) For instance, addition of Me_3SiCN to aldehydes [28], for *Diels-Alder* additions [29–31], for hetero-*Diels-Alder* reactions (Si-enolether + nitroolefins [32]), and R_2Zn additions to nitrostyrenes [33], *Michael* additions [34], and for iodolactonizations [35].

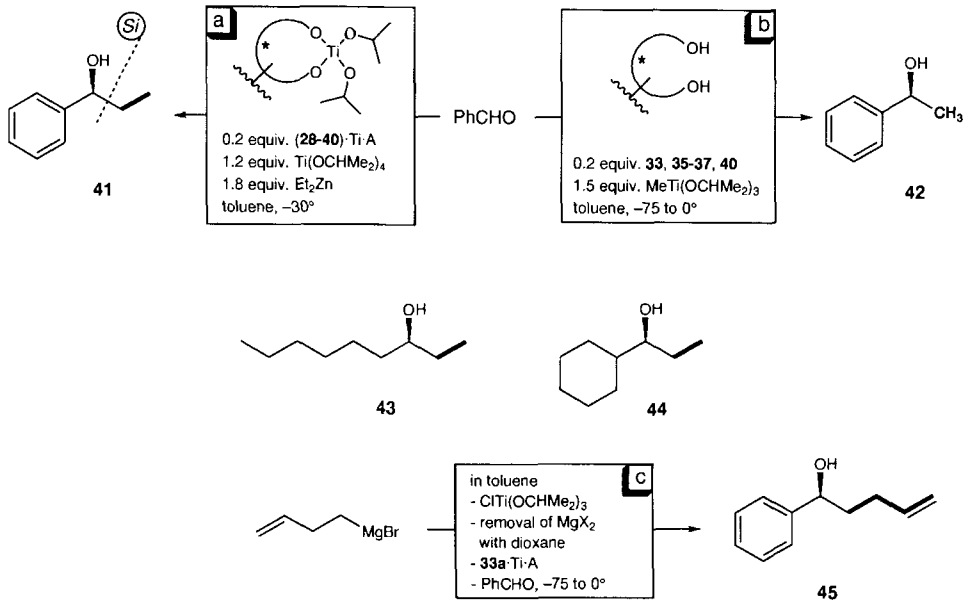
[12]) Useful catalytic applications not referred to in the reviews [5] [6] are for instance *Diels-Alder* reactions of sulfonyl-enones [36], and of keto-enones [37], cyclopropanations [38], R_2Zn additions [39], and borane reductions of ketones [40].

filtration, in this case[13]). The enantioselectivities depend very little upon the nature of the aryl group on the TADDOL moiety (except for α-naphthyl **34**, and like with the soluble TADDOLs), upon the type of polymer (except for Type V **40**·Ti·A, the 'branching TADDOL'), upon the degree of functionalization, and upon the level of cross-linking. As in solution, the selectivity drops drastically when less then 5% Ti-TADDOLate is present.

The advantages of the polymer-bound TADDOLs for the reactions shown in *Scheme 5* are evident from the following facts: *i*) they can be separated by simple filtration; *ii*) the polymer-bound titanates are quite stable and can be used several times, by decanting the supernatant product alkoxide solution, and replacing it – after washing the polymer – by a new reactand solution; with the polymer **33a**·Ti·A, this was done four times, with essentially no decrease of enantioselectivity (*Fig. 3*); *iii*) the polymer, recovered after acidic aqueous workup, careful washing, and drying, can be 'titanated' and used again, with no loss of enantioselectivity (see **33a**·Ti·A 'recycl.', → **41**, *Table 1*). Thus, neither treatment with $Ti(OCHMe_2)_4$ nor the acidic decomposition of the polymer-bound Ti-TADDOLate complex, the precipitating TiO_2·aq., or water had detrimental effects on the polymer's properties in this experiment!

The typical catalysts for enantioselective R_2Zn additions, the amino alcohols, have been attached to polymers by a number of authors[14]).

Scheme 5. *Nucleophilic Additions of R_2Zn or $RTi(OCHMe_2)_3$ to Aldehydes Using Catalytic Amounts of Polymer- and Dendrimer-Bound Ti-TADDOLates to Give Products* **41**–**45**. The relative topicity of the additions is the same as under homogeneous conditions. For yields and selectivities, see *Table 1*.



[13]) On SiO_2, the dendrimers **28**–**31** do not move with Et_2O/pentane eluent, they can be recovered from the column with $AcOEt/CH_2Cl_2$.

[14]) A review article is published in *Houben-Weyl* on stereoselective synthesis [46]. For some current examples, see [47].

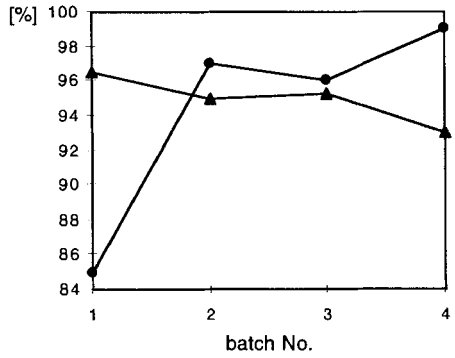


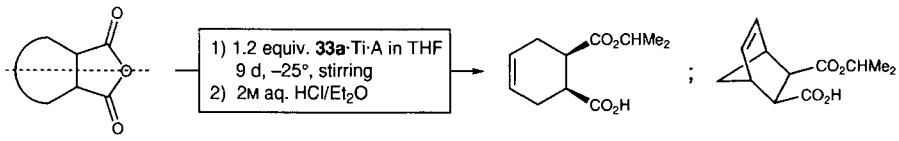
Fig. 3. *Yield and enantioselectivity for multiple formation of (S)-***41** *under the conditions* (a) *in* Scheme 5, *using the Type-II polymer* **33a**·Ti·A. Reaction time 18 h. After each run (2.25-mmol scale), the solution was removed by syringe, the polymer rinsed twice with toluene, and then new reactands were added. –●–: % yield; –▲–: enantiomer purity of **41** (% (*S*)).

Table 1. *Yields and Selectivities of Nucleophilic Additions to Aliphatic and Aromatic Aldehydes Using* R_2Zn (Method *a*) *or* $RTi(OCHMe_2)_3$ (Method *b* and *c*), *and Catalytic Amounts of Polymer-* (Type I–V) *or Dendrimer-Bound Ti-TADDOLates* (**20**–**40**)·Ti·A. See equations in *Schemes 4* and *5*. The enantiomer ratios in the products **41**–**45** were determinded by GC on chiral columns (as described previously [41–45]).

		Product	Method	Yield [%]	(*S*)/(*R*)
Soluble	**2**	**41**	*a*	90	64:36
TADDOLs	**3**	**41**	*a*	99	99.5:0.5
	5	**41**	*a*	95	98.5:1.5
	1	**42**	*b*	82	98:2
	5	**43**	*a*	91	98:2
	5	**44**	*a*	64	96.5:3.5
	1	**45**	*c*	52	99:1
Dendrimers	**28**	**41**	*a*	61	99:1
	29	**41**	*a*	98	98.5:1.5
	30	**41**	*a*	54	98:2
	31	**41**	*a*	26	97:3
Polymers Type I	**32**	**41**	*a*	97	99:1
	ent-**32**	**41**	*a*	92	2:98
Polymers Type II	**33a**	**41**	*a*	97	97.5:2.5
	33a	**41**	*a*, recycl.	76	97.5:2.5
	33a	**41**	*a*, 0.05 equiv.	96	90:10
	33b	**41**	*a*	93	97.5:2.5
	33c	**41**	*a*	96	98.5:1.5
	33d	**41**	*a*	95	98.5:1.5
	33e	**41**	*a*	96	98.5:1.5
	33f	**41**	*a*	97	98.5:1.5
	34	**41**	*a*	94	77.5:22.5
	35	**41**	*a*	99	98:2
	36	**41**	*a*	95	98:2
	37	**41**	*a*	96	97:3
	33a	**42**	*b*	70	93.5:6.5
	35	**42**	*b*	64	92:8
	36	**42**	*b*	74	96.5:3.5
	37	**42**	*b*	67	95:5
	33a	**43**	*a*	75	96:4
	33a	**44**	*a*	57	93:7
	33a	**45**	*c*	40	96:4
Polymer Type III	**38**	**41**	*a*	98	98.5:1,5
Polymer Type IV	**39**	**41**	*a*	96	96.5:3.5
Polymer Type V	**40**	**41**	*a*	96	87.5:12.5
	40	**42**	*b*	77	86:14

5.2. *Enantioselective Alcoholysis of* meso-*Anhydrides by Stoichiometric Me_2CHO Transfer from Polymer-Bound Ti-TADDOLates.* Next, we tested the enantioselective ring opening of a bicyclic and a tricyclic achiral anhydride using the Type II TADDOLate **33a**·Ti·A, carrying 0.63 mmol TADDOL/g polymer. Since this is a stoichiometric reaction, *ca.* 1.5 g of the functionalized polymer had to be used for a 0.8-mmol run. The products from maleic-anhydride addition to butadiene and cyclopentadiene were dissolved in THF and stirred with **33a**·Ti·A for 9 d (a slow reaction also under homogeneous conditions! [25]) to give the monoesters **46** and **47** of high enantiomer purity (*Scheme 6*). While the reaction was somewhat slower than under homogeneous conditions (9 d for 35% conversion to **46** and 85% to **47**, *cf.* [25]), the relative topicity was the same, and the selectivities were identical within experimental error[15]).

Scheme 6. *Enantioselective Ring-Opening of Two Cyclic* meso-*Anhydrides with 20% Excess* **33a**·Ti·A. The enantiomer ratios were determined as reported in [25].



meso-anhydride

46
35% yield
e.r. > 95 : 5

47
85% yield
e.r. 98 : 2

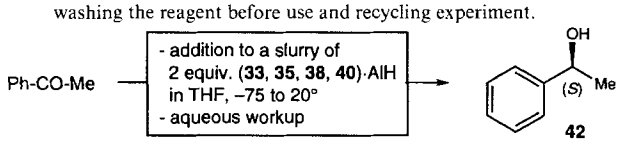
5.3. *Acetophenone Reduction with the Polymer-Bound TADDOLate-Modified $LiAlH_4$ Derivatives* (**33**, **35**, **38**, **40**)·*AlH.* The polymer-bound modified LAH[16]) was used with the same 2:1 stoichiometry as the analogous soluble one. The results of the essentially quantitative reductions (→ **42**) are collected in *Table 2.* Again, the polymers to which the Al-TADDOLate is attached without (Type II) or with spacer (Type III), but not the one with 'branching TADDOLates' (Type V), gave results identical within experimental error to those obtained in solution [7] [8]. Due to the two-fold excess of the stoichiometric polymer-bound reagent, the amount of solvent necessary to keep the reaction mixture stirrable is five times as large as under homogeneous conditions. It is important to wash the polymer-bound reagent twice with THF before use. Again, the recovered polymer can be used for preparing the reagent at least once more, without prejudicial effects to this enantioselective reduction (see entry **33a**·AlH, 'recycl.' in *Table 2*).

5.4. Diels-Alder *and [3 + 2] Addition of 3-Crotonoyl-oxazolidin-2-one to Cyclopentadiene and* N-*Benzylidenephenylamine* N-*Oxide Catalyzed by* (**32**–**40**)·*Ti*·*B.* Since the first report on Ti-TADDOLate-mediated *Diels-Alder* additions [29] [50] of α,β-unsaturated carboxylic-acid derivatives, this reaction was studied intensively by many groups, and it was found that very high enantioselectivities can be achieved by employing either excess

[15]) This experiment is a test of the properties of polymer-bound Ti-TADDOLates, rather than a practical alternative to the analogous reaction in solution, because product isolation (by alkaline extraction of the half ester) and separation from the TADDOL is not causing any problems in this case.

[16]) Again, there are many previous reports on polymer-bound complex hydrides and boranes for enantioselective reductions of ketones; see the review articles [48] and most recent papers [49].

Table 2. *Yields and Enantiomer Ratios* (e.r.) *of 1-Phenylethanol Obtained by Acetophenone Reduction with Various Polymer-Bound TADDOLate Aluminium Hydrides.* Comparison with the homogeneous reaction [7] [8]; effect of washing the reagent before use and recycling experiment.



			Conversion [%]	(*S*)/(*R*)
Soluble TADDOLs	**3**		92	87:13
	5		83	95:5
Polymers Type II	**33a**	no washing	95	78:22
	33a		75	88:12
	33a	recycl.	90	86:14
	33c		95	83:17
	35	no washing	98	75:25
Polymer Type III	**38**		65	82:18
Polymer Type V	**40**		85	72:28

[31] or catalytic [51] amounts of the chiral *Lewis* acid[17]). Mechanistic investigations have been reported [2] [53–55], and a rule for the stereochemical course of the reaction has been derived [2] [5]. The enantioselective *Lewis*-acid catalysis of [3+2] cycloadditions, on the other hand, has been the subject of only three very recent investigations [56–58], one of which involved the use of a Ti-TADDOLate [57]. To the best of our knowledge, the use of polymer-bound chiral *Lewis* acids for *Diels-Alder* reactions has been reported only by *Itsuno et al.* [59].

We have now used *ca.* 0.2 equiv. of polymer- or dendrimer-bound Ti-TADDOLates (**28**–**40**)·Ti·B for catalyzing the cycloadditions of 3-crotonoyl-1,3-oxazolidin-2-one to cyclopentadiene (→ **48**, *Scheme 7, a*, and *Table 3*) and to (*Z*)-*N*-benzylidenephenylamine *N*-oxide (→ **49**, *Scheme 7, b*, and *Table 4*).

The data in *Table 3* show that *i*) except for the Ti-TADDOLates bonded to *Merrifield* resin (Type I), all polymer-bound *Lewis* acids catalyze the *Diels-Alder* addition equally well (the rate of reaction is approximately the same as in solution!); *ii*) the same (1*S*,2*S*,3*R*,4*R*)-stereoisomer is formed preferentially as in solution with all TADDOLates but one; *iii*) there is a reversal of the stereochemical course, as under homogeneous conditions [2], when the α-naphthyl-TADDOLate (**2**·Ti·B and **34**·Ti·B) is used; *iv*) the enantioselectivities with which the *endo*-adduct **48** is formed (e.r. ≤ 4:1) are much lower than with the soluble TADDOLates (e.r. ≤ 19:1; see the discussion in *Chapt. 6*); *v*) otherwise, the enantioselectivity depends very little upon the particular structure of the TADDOLate moiety and type of polymer; *vi*) the addition of molecular sieve gives rise to only a small improvement of the enantioselectivity (like in solution [2]). We have also tested the stability of the polymer-bound *Lewis* acid with the *Diels-Alder* reaction using the Ti-TADDOLate **33a**·Ti·B: after the reaction was completed, the supernatant solution was decanted, the polymer beads washed with toluene, a fresh crotonoyl-oxazolidinone solution and 20 equiv. of cyclopentadiene added at room temperature, and the procedure repeated after 1 h. As can be seen from *Fig. 4*, the degree of conversion, the

[17]) The 'best' chiral *Lewis* acids for various *Diels-Alder* reactions have been reported by the groups of *Corey* and *Evans*, see references in the review articles [52].

Scheme 7. Diels-Alder *Addition* (a) *and [3 + 2] Cycloaddition* (b) *of 3-Crotonoyloxazolidinone to Cyclopentadiene and a Nitrone in the Presence of 0.2 Equiv. of Polymer- or Dendrimer-Bound Ti-TADDOLate.* The structure, including the absolute configuration of the main product **48** from the *endo* [4 + 2] addition, has been derived by *Narasaka et al.* [51]. The relative configuration of the major [3 + 2] adduct **49** follows from a crystal structure of the minor adduct [57]; the absolute configuration of **49** shown is assigned herein, because it is compatible with the fact that Ti-TADDOLate-activated oxazolidinone derivatives of α,β-unsaturated acids combine with nucleophiles preferentially from the *Re*-face of the α-carbonyl trigonal center (this is true not only for *Diels-Alder* reactions but also for [2 + 2] cycloaddition and for ene reactions; for a list of examples with references, see [2]).

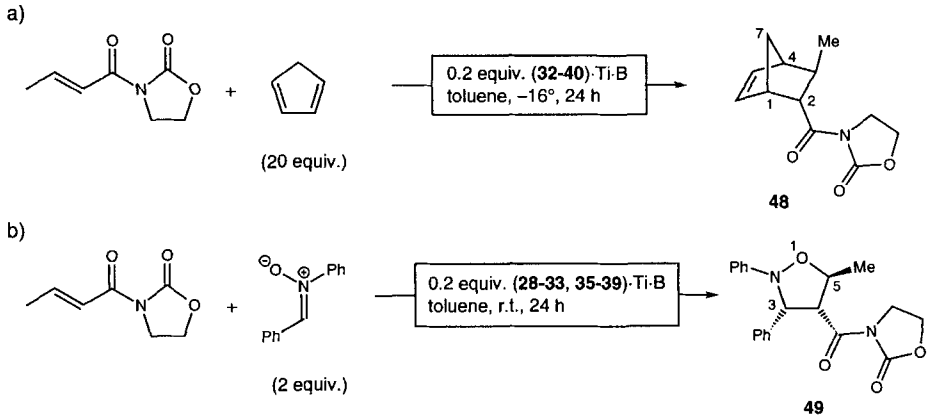


Table 3. Diels-Alder *Additions with Formation of the* endo-*Adduct* **48** *and the Diastereoisomeric* exo-*Adduct, Catalyzed by Soluble and Polymer-Bound Ti-TADDOLates* (see *Scheme 7, a*). The diastereoisomer and enantiomer ratios (*endo*/*exo* and e.r.) were determined as described in [2]. The yields given in parentheses have been determined by NMR, all other yields refer to chromatographically purified products. If not stated otherwise, the reaction mixture was kept at –16° for 24 h before workup.

TADDOL Used		Reaction temp./time	Product **48**			
			Yield [%]	*endo*/*exo*	e.r.	
					endo	*exo*
Soluble	**2**		58	89:11	14:86	17:83
	3		94	87:13	94:6	89:11
	5		82	83:17	69:31	45:55
Polymers Type I	**32**	0°/2 d	(< 5)	–	–	–
	ent-**32**	0°/2 d	(< 5)	–	–	–
Polymers Type II	**33a**		76	82:18	63:37	57:43
	33a	0°/16 h	92	81:19	60:40	54:46
	33a	25°/3 h	94	79:21	59:41	53:47
	33b		84	83:17	63:37	58:42
	33c		63	83:17	65:35	55:45
	33c	Mol. sieves (4 Å)	69	85:15	68:32	51:49
	33d		48	84:16	63:37	56:44
	33e		(52)	82:18	60:40	65:35
	33f		(32)	86:14	60:40	60:40
	34		(40)	85:15	29:71	28:72
	35		92	87:13	78:22	63:37
	35	0°/20 h	97	85:15	73:27	57:43
	36		64	83:17	60:40	50:50
	37		60	86:14	65:35	52:48
Polymer Type III	**38**		(56)	82:18	58:42	62:38
Polymer Type IV	**39**		(56)	83:17	62:38	60:40
Polymer Type V	**40**		(30)	81:19	53:47	60:40

Table 4. *[3 + 2] Cycloadditions with Formation of the* exo-*Adduct* **49** *and the* endo-*Diastereoisomer (trans-trans) Catalyzed by 0.2 Equiv. of Soluble, Polymer-, or Dendrimer-Bound Ti-TADDOLates* (see *Scheme 7, b*). The diastereoisomer ratio was determined by NMR, the enantiomer ratio in the *exo*-product by ^{1}H-NMR in the presence of chiral shift reagent as reported by *Jørgensen* and coworkers [57]. The numbers in the very first entry are taken from [57]. The yields given in parentheses have been determined by NMR, the other yields refer to chromatographically purified products. If not stated otherwise, the reaction time was 24 h at room temperature.

			Poduct **49**		
			Yield [%]	*exo*/*endo*	e.r. *exo*
Soluble TADDOLs	**1**		(72)	89:11	77:23
	1	(0°/20 h)	94	90:10	79:21
	1	(−5°/2 d)	(82)	94:6	82:18
	2		(99)	90:10	50:50
	3		(61)	87:13	76:24
	4		(81)	92:8	75:25
	5		(92)	94:6	75:25
Dendrimers	**28**		(75)	86:14	72:28
	29		(56)	86:14	70:30
	30		45	85:15	73:27
	31		54	83:17	74:26
Polymer Type I	**32**		(37)	76:24	50:50
Polymer Type II	**33a**		66	91:9	76:24
	35		86	92:8	70:30
	36		62	90:10	78:22
	37		58	90:10	75:25
Polymer Type III	**38**		(52)	87:13	66:34
Polymer Type IV	**39**		64	86:14	69:31

diastereoselectivity (*endo*/*exo*), and the enantioselectivity with which the *endo*- and the *exo*-products were formed hardly changed after nine runs (each on the usual 2-mmol scale); this result suggests that our polymer-bound *Lewis* acid might be used in flow reactors with long life times!

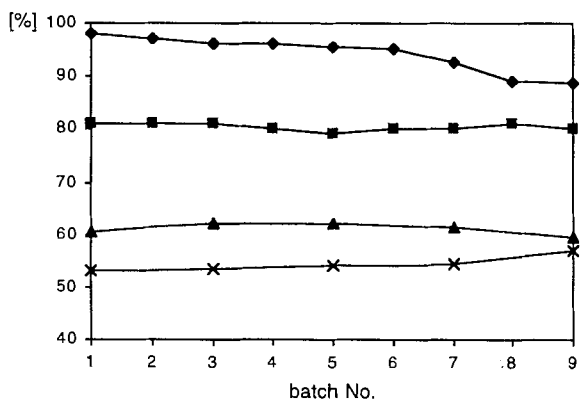


Fig. 4. *Conversion and stereoselectivities of the* Diels-Alder *addition shown in* Scheme 7, a, *with multiple use of the same crop of Ti-TADDOLate beads* **33a** · *Ti* · *B*. The reaction was carried out on a 2-mmol scale at room temperature (comparison with the results obtained at −16 and 0° (*Table 3*) shows that there is a rather small temperature effect on the selectivities). The enantiomer ratios (given here as % of the excess enantiomers, in order to have a common *y*-axis in the diagram), were determined in every second run. –◆–: % conversion; –■–: % *endo*; –▲–: %of major enantiomer in *endo*-product; –×–: % of major enantiomer in *exo*-product.

For the [3 + 2] cycloaddition (*Scheme 7, b*), we first tested different soluble Ti-TADDOLates for comparison with the published data [57] to find that, in the catalytic version of the reaction, there is hardly any influence of the temperature and of the TADDOL aryl groups on the yield, diastereo-, or enantioselectivities, except that the α-naphthyl-TADDOL gives totally racemic product **49** (first 7 entries in *Table 4*). With the dendritic and the polymer-bound dichloro-Ti-TADDOLates, the yields are generally somewhat lower, but, again, the selectivities are almost the same as in solution (exception: the *Lewis* acid attached to *Merrifield* resin (Type I) gives *rac*-product **49**[18]). Information about the d.r. and e.r. determinations and structural assignments of product **49** is given in *Scheme 7* and *Table 4*.

For a mechanistic discussion of enantioselective catalysis by metal complexes, it is important to know whether the enantiomer purities of the catalyst and of the product have a linear or a nonlinear relationship [60–62][19]). We have, therefore, determined the enantioselectivity of the isoxazolidine **49** formation with the soluble dichloro-β-naphthyl-Ti-TADDOLate of four different enantiomer purities (*Fig. 5, a*) and compared it with the corresponding data for the *Diels-Alder* reaction (*Fig. 5, b*). Clearly, the [3 + 2] cycloaddition shows a linear, the [4 + 2] a nonlinear relationship (positive effect)[20]).

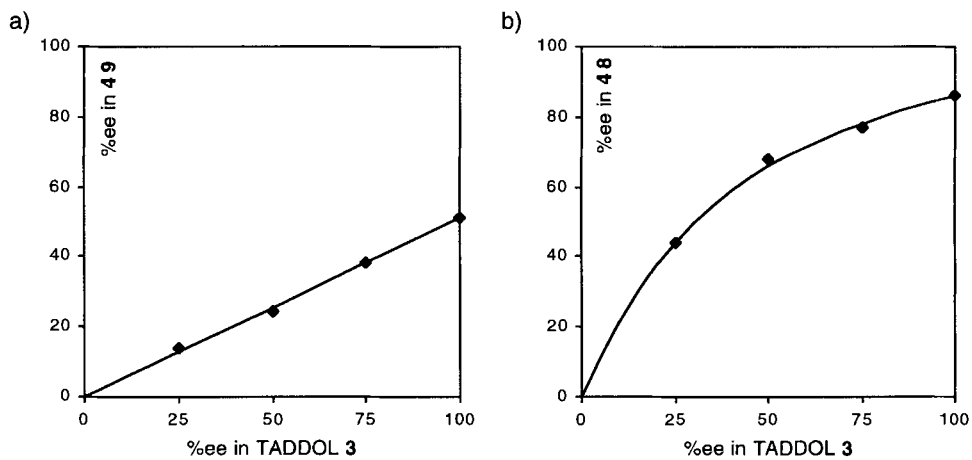


Fig. 5. *Relationship between the enantiomer purities of the products and of the β-naphthyl-TADDOL* **3** *used in the homogeneous catalysis for the [3+2] (a; →***49***) and [4+2] cycloadditions (b; →***48***).* The reaction leading to **49** was carried out as specified in *Scheme 7, b*, and *Table 4*. The data for the *Diels-Alder* reaction are taken from [2]; using the equations for model 1 of the ML_2 system (*Kagan et al.*, supplementary material with [61]), a *g* value of 0.3 (rate of reaction involving two homochiral TADDOLs is three times larger than with two heterochiral TADDOLs) and a *K* value of 300 reproduce the curve in diagram *b*) perfectly.

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[18]) The dichloro-Ti-TADDOLate of **3** catalyzes the [2 + 2] cycloaddition of 1-(methylthio)hex-1-yne to 2-acryloyl-1,4-oxazolidinone (see the reference to *Narasaka*'s work in [2]) with higher enantioselectivity (e.r. 80:20) than the polymer-bound **33a** · Ti · **B** (e.r. 63:37); both give the (*R*)-product preferentially (following *Narasaka*'s assignment).

[19]) See also comments in Footnote 11 of [26].

[20]) We hesitate to use the term 'chiral amplification', because it is hard to see how 'amplification' could be non-congruent with its mirror image.

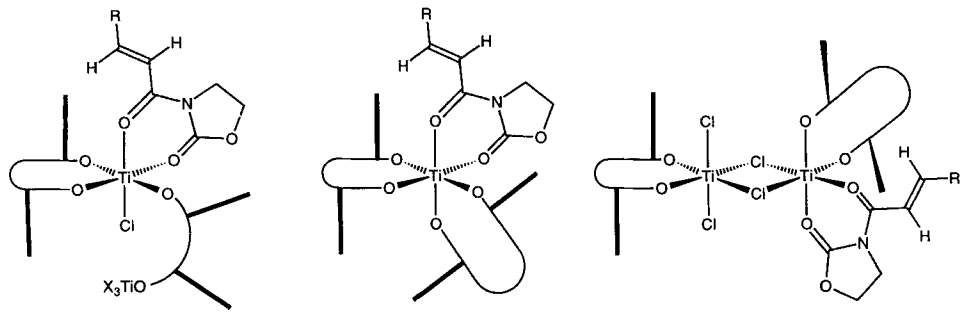
6. Discussion and Conclusions. – The examples, described herein, for the use of the new polymer-bound Ti-TADDOLates as chiral *Lewis* acids demonstrate that there is a surprising resemblance of the activities and selectivities with those observed in homogeneous solution. Especially the most easily prepared polymers of Type II, which have no spacer between the benzene ring at C(3) of the dioxolane and the polymer chain, turn out to perform well. Less successful is the polymer in which the diarylmethanol unit of the TADDOL is attached, in a cross-linking way, to the polymer network. Also, the TADDOLate-modified *Merrifield* resin fails to give useful *Lewis*-acid catalysts in some cases. The great stability of the complexes of polymer-bound TADDOLs with Ti allows for multiple uses, and we are in the process of building a simple reactor, with the TADDOL-containing polymer beads in a container such that reactant and product solutions can be exchanged many times without replacing the catalyst. Removal, and thus renewal or exchange, of the metal centers without loss of a large fraction of the TADDOL moieties in the polymer has also been demonstrated (*Sect. 5.1* and *5.3*); this possibility makes the polymer-bound TADDOLs even more attractive materials. Furthermore, the TADDOLs are H-bond donors and have been shown to form complexes in solution (use as chiral NMR shift reagents [63]) and in the solid state (enantioselective clathrate formation [64]); this property suggests that TADDOL-containing polymers may be used as stationary GC and HPLC phases for enantiomer separation on analytical and/or preparative scale. Some of these possibilities are presently being tested in our laboratories.

What is the catalytically active species in TADDOLate Lewis-*acid catalysis?* The poor performance of the polymer-bound as compared to the soluble Cl_2Ti-TADDOLate in the *Diels-Alder* reaction (*Scheme 7, a*), together with the observed nonlinear relationship between TADDOL and product enantiomer purity (*Fig. 5, b*) in this cycloaddition, when carried out in solution, suggest that at least two TADDOL molecules are involved in the step determining the enantioselectivity. Such a cooperation of sites is impossible or at least less likely with the polymer-bound Ti-TADDOLates. What is known about the mechanism of this catalysis, and how could this cooperation of two TADDOLate units or of two of the corresponding Ti-complexes come about? The latter question has not been addressed so far – the nonlinearity has simply been ignored in previous mechanistic discussions [2] [51] [53–55] [65] [66]. Let us consider four possible active complexes **A**, **B**, **C**, and **D** in *Fig. 6*, remembering that the actually observed course of the reaction is such that the cyclopentadiene, like other nucleophiles [2], approaches from the *Re*-face of the trigonal center in the α-carbonyl position. Only the cationic complex **D** with a second TADDOLate in the *gegenion* accounts for the nonlinearity of the enantioselectivity[21][22][23][24][25][26]. The rules for ligand exchange, ligand permutation, and ligand bond-

[21] Neutral complexes with octahedral ligand spheres of Ti, containing two TADDOLate units, such as **I**, **II**, and **III**, would, of course, also account for the observed nonlinearity (see *Fig. 5*). We do not expect, however, that the *Lewis* acidity of the position bearing the O=C–C=C moiety would be increased in those complexes: $ClTi(OCHMe_2)_3$ (*cf.* **I**) is a much weaker *Lewis* acid, catalyzing the reaction leading to **48** far worse than $Cl_2Ti(OCHMe_2)_2$; the spiro-titanate (*cf.* **II**) $Ti(TADDOLate)_2$, which is stable in air, does not catalyze the *Diels-Alder* reaction, studied herein, at all, it contains a highly hindered Ti center providing a very poor catalytic site [44]; the increasing activity of Ti-TADDOLates with increasing steric hindrance is not compatible with such an associative cooperation of two TADDOLates (*cf.* **I**, **II**, **III**); thus, the *Diels-Alder* reaction at

ing order on apical and equatorial positions of trigonal bipyramids such as **D** are well defined by the *Walsh-Bent-Muetterties* [69–72] polarity [73] or apicophilicity [74] rule. According to this rule, the most electronegative ligand Cl in **D** exerts the strongest electron-withdrawing effect in the *trans*-apical position on the trigonal bipyramid. This effect, together with the decrease of steric crowding when going from octahedral to trigonal bipyramidal coordination (**C** → **D**), and the introduction of a positive charge[27]) on Ti in complex **D** will tremendously increase the reactivity towards nucleophiles of the C=C bond in the oxazolidinone derivative. In fact, we have shown that addition of $AgClO_4$ to the homogeneous reaction mixture containing the Cl_2Ti-TADDOLate from **1** leads to a great acceleration of the rate of formation of the *Diels-Alder* adduct **48** (reaction temperature −75° instead of 0°!)[28]). In previous mechanistic discussions, we have interpreted the *ligand acceleration*[29]) exerted by the TADDOLate ligand, as com-

Cont.



I II III

hand occurs with about equal rate with the Cl_2Ti-TADDOLate from **1** (Ph_4) at 0° as it does with the analogous β-naphthyl derivative (from **2**) at −20° (see Footnote 50 in [2]).

[22]) The complex geometry proposed by *Corey* and *Matsumura* [65a] has an unfavorable s-*trans*-conformation around the O=C–C=C bond and a π-stacking interaction of the electrophile π-system with a *quasi*-equatorial benzene ring of the diarylmethanol unit.

[23]) A bonding order of ligands on hexacoordinate Ti-centers was derived from X-ray crystal structures by *Gau et al.* [67]; in this paper, the authors also discuss the relative rates of ligand exchanges on octahedral Ti complexes.

[24]) For a general discussion of *trans*-effects on the stability and reactivity of transition metal complexes, see [68].

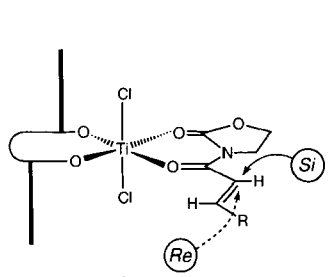
[25]) Removal of a Cl-atom from both **B** and **C** could lead to the same cation **D**: interchange of the apical carbonyl O-atom and Cl in **D** leads to an identical structure, due to the C_2 symmetry of the TADDOLate ligand.

[26]) The possibility that cationic Ti complexes might actually be the catalytically active species has been previously mentioned (for the *Diels-Alder* reaction see Chapt. 5 and Footnote 75b in [2]) or proposed (for the opening of *N*-(methylsulfonyl)imides [26]) by us, and by others [65b].

[27]) Although the conditions under which Ti-TADDOLate-mediated reactions are carried out (low temperature and non-polar solvents such as hexane, toluene, CH_2Cl_2, THF) do not favor ionic dissociations; the complex ions involved (*cf.* **D** in *Fig. 6*) are probably stable and hydrophobic enough to be formed in the small amounts, which might be necessary for catalysis.

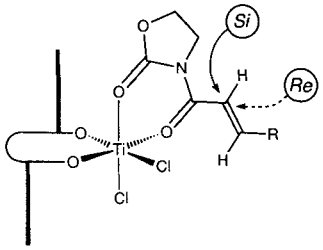
[28]) For details about this experiment, see Footnote 46 in [2] and [32].

[29]) This term was originally proposed by *Sharpless* in a strictly phenomenological sense. In the meantime, mechanistic interpretations have been put forward in many cases (such as for the Ti-TADDOlates [2] [44] [45]). For a timely review article on ligand acceleration, see [75].



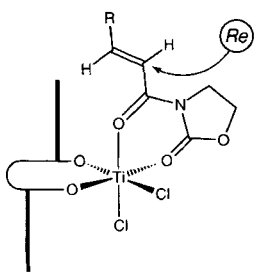
A

- X-ray crystal structure (*Jørgensen* [54])
- most abundant species in solution (*DiMare* [53] [66])
- least activated C=C bond
- bias between the two double bond faces not pronounced



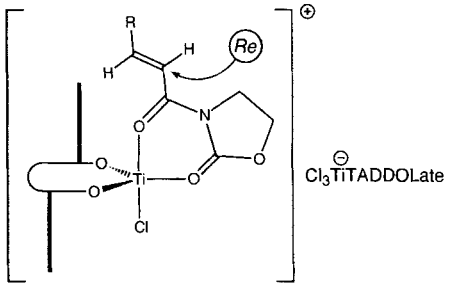
B

- third most abundant species in solution (*DiMare* [53] [66])
- second to least activated C=C bond
- reacts faster with a diene than **A** (*DiMare* [66])
- would not be expected to give observed product



C

- second most abundant species in solution (*DiMare* [53] [66])
- second highest activation of double bond (proposed previously as the product-forming complex [2] [53])
- reacts more rapidly with a diene than **A** (*DiMare* [66])
- would give observed product



D

- cationic complex (proposed herein)
- not detected so far
- by far greatest activation of C=C bond
- would give observed product
- compatible with non-linearity of % ee TADDOL *vs.* product **48**

Fig. 6. *Four complexes* **A–D** *of Ti-TADDOLate with 3-enoyl-1,3-oxazolidinones.* The neutral octahedral complexes **A–C** (R = H, Me, Pr, Bu, Ph) have been found to be present in crystals and in solution. The heavy vertical lines in **A–D** are meant to indicate the *quasi*-axial aryl groups on the (*R,R*)-TADDOL moieties.

pared to BINOLate and isopropoxides on Ti[30]), by invoking sterically induced fast dynamics of exchange of ligands, such as solvent molecules and substrates to be activated for reactions on the – preferentially hexacoordinate – Ti center [44]. The proposal, put forward now, of a dissociative (ionizing) rather than associative (neutral) ligand-exchange process, and, thus, substrate activation, may turn out to be a viable mechanistic

[30]) Examples are: *i*) The nucleophilic addition of $RTiX_3$ or R_2Zn to aldehydes, acceleration by Ti-TADDOLate *vs.* $Ti(OCHMe_2)_4$ ≥ 50:1 [45]. *ii*) Ring opening of cyclic anhydride by $(Me_2CHO)_2$Ti-TADDOLate *vs.* $(Me_2CHO)_4$Ti 5:1 [25] [76]. *iii*) Ring opening of a cyclic *meso*-anhydride is faster (≥ 5:1) with $(Me_2CHO)_2$Ti-TADDOLate than with $(Me_2CHO)_2$Ti-BINOLate [77]. *iv*) Ring opening of cyclic *N*-(methylsulfonyl)imides by $(Me_2CHO)_4$Ti is much slower than by $(Me_2CHO)_2$Ti-TADDOLate [26].

model for other Ti-TADDOLate-mediated reactions as well[31])[32]). In this regard, it is intriguing to note that the secret of the highly efficient Cp_2Zr-type catalysts for olefin polymerization has been shown in a masterly study by *Brintzinger et al.* [79] to be the formation of highly electrophilic, cationic complexes Cp_2Zr^+-CH_2R, which are the actual chain-propagating sites.

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Experimental Part

1. *General.* Reagents: $(i\text{-PrO})_3TiMe$ [1], $(i\text{-PrO})_2TiCl_2$ [2], 2M stock soln. of $ZnEt_2$ [41] were prepared following reported procedures. The TADDOLs **1**–**5** were synthesized according to [8] [63a] [80]. All other commercially available chemicals used were of *puriss p.a.* quality, or purified and dried according to standard methods. TLC: precoated silica gel *60 F_{254}* (*Merck*); visualization by irradiation with UV light or detection by phosphomolybdic acid soln. (phosphomolybdic acid (25 g), $Ce(SO_4)_2 \cdot H_2O$ (10 g), H_2SO_4 (60 ml), and H_2O (940 ml)). Flash chromatography [81] (FC): SiO_2 *60* (0.04–0.063, *Fluka*). Capillary gas chromatography (CGC): *Carlo Erba HRGC 5160* or *Carlo Erba FRACTOVAP 4160* with integration by means of a *Carlo Erba DP 700 CE* data processing unit; column (*Macherey-Nagel*): *a*) *FS-Hydrodex β-PM* (50 m × 0.25 mm ID); *b*) *FS-Hydrodex β-3P* (50 m × 0.25 mm ID); *c*) *FS-Lipodex E* (*γ-CD*, 50 m × 0.25 mm ID); carrier gas was H_2. Bulb-to-bulb distillation: *Büchi GKR 50*. B.p. correspond to uncorrected air-bath temp. M.p.: open glass capillaries; *Büchi 510*. $[\alpha]_D$ at r.t. (*ca.* 20°); *Perkin-Elmer 241* polarimeter; *p.a.* solvents. IR ($CHCl_3$): *Perkin-Elmer 1600 FTIR*, $\tilde{\nu}$ in cm^{-1}. NMR Spectra: *Bruker AMX-II 500*, *Bruker AMX 400*, *WM 300*, *Varian XL 300*, *Gemini 300*, or *Gemini 200*. δ in ppm rel. to Me_4Si (= 0 ppm), J in Hz; unless stated otherwise, $CDCl_3$ soln.; C-multiplicities were assigned by DEPT techniques. MS: *VG Tribrid* spectrometer (EI), *VG ZAB2-SEQ* with 3-nitrobenzyl alcohol (FAB; 3-NOBA), or *Bruker Reflex* spectrometer (positive-ion mode) with α-cyano-4-hydroxycinnamic acid (MALDI-TOF; CCA); fragment ions in m/z with rel. intensities (%) in parentheses. Elemental analyses were performed by the Microanalytical Service of the Laboratorium für Organische Chemie, ETH-Zürich.

2. *Preparation of the TADDOLs* **18**–**26**. *1-(4-Ethenylphenyl)ethanone Dimethyl Ketal* (**9**): A soln. of *4-ethenylphenyl methyl ketone* [82] (**7**; 4.0 g, 27.5 mmol) in MeOH (12.5 ml) was treated with $HC(OMe)_3$ (3.0 ml, 27.5 mmol) and $TsOH \cdot H_2O$ (5 mg). After stirring for 30 min at r.t. additional $HC(OMe)_3$ (3.0 ml, 27.5 mmol) was added. After 1 h, the mixture was diluted with 1M NaOH (40 ml), extracted with Et_2O, washed with sat. aq. NaCl soln., dried ($MgSO_4$), and evaporated to give **9** (5.25 g, 99%), which was used without further purification. ^{1}H-NMR (200 MHz): 1.54 (*s*, Me); 3.20 (*s*, 2 MeO); 5.25 (*dd*, J = 0.9, 10.9, 1 vinyl. H); 5.77 (*dd*, J = 0.9, 17.7, 1 vinyl. H); 6.73 (*dd*, J = 10.9, 17.7, 1 vinyl. H); 7.44 (*m*, 4 arom. H).

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[31]) Inspite of the linear correlation between enantiomer purities of TADDOL and product in the case of R_2Zn addition to aldehydes in the presence of $(Me_2CHO)_2$Ti-TADDOLate/$(Me_2CHO)_4Ti$ [41], or in the case of imide ring opening by $(Me_2CHO)_2$Ti-TADDOLate [26], or in the [3 + 2] cycloaddition described herein (*Fig. 5, a*), cationic complexes could be involved; the anionic counterions may have no or very different effects on the reactivity of the cation, as compared to the *Diels-Alder* reaction studied here (*Scheme 7, a*, and *Fig. 5, a*; *cf.* also [60–62]).

[32]) Cationic complexes may or may not be involved as the actual catalytic species in other reactions mediated or catalyzed by metal complexes of TADDOLates (for lists of references to such reactions, see [1–7] [78]). How different the stereochemical courses of these reactions may actually be, is evident from a recent paper by *Greeves et al.* [23b] who use alkyl Ce-TADDOLates for nucleophilic additions to aldehydes with relative topicity *lk* (the (*R,R*)-TADDOLate causes *Re*-addition), in contrast to *all* reported analogous reactions involving Ti-(*R,R*)-TADDOLates or (*P*)-BINOLates which lead to *Si*-addition (see [2] [44] [45] and references cited therein).

(4-Ethenylphenyl)phenylmethanone Dimethyl Ketal (**10**): A soln. of *4-ethenylphenyl phenyl ketone* [83] (**8**; 5.7 g, 27.5 mmol) in MeOH (12.5 ml) was treated with $HC(OMe)_3$ (6.0 ml, 55.0 mmol) and $TsOH \cdot H_2O$ (5 mg). After stirring for 6 h at reflux, the mixture was diluted with 1M NaOH (40 ml), extracted with Et_2O, washed with sat. aq. NaCl soln., dried ($MgSO_4$), and evaporated to give crude **10** (6.5 g, contains *ca.* 15 mol-% **8**), which was used without further purification. ^{1}H-NMR (200 MHz): 3.14, 3.34 (2*s*, 2 MeO); 5.21 (*d*, J = 10.9, 1 vinyl. H); 5.72 (*d*, J = 17.6, 1 vinyl. H); 6.68 (*dd*, J = 10.9, 17.6, 1 vinyl. H); 7.21–7.37, 7.43–7.54 (2*m*, 9 arom. H).

Dimethyl (4R,5R)-2-(4-Ethenylphenyl)-1,3-dioxolane-4,5-dicarboxylate (**11**). Following the procedure described in [80], to a soln. of (*R,R*)-dimethyl tartrate (27.5 g, 154.6 mmol) and *4-ethenylbenzaldehyde* [84] (**6**; 17.0 g, 128.8 mmol) in AcOEt (250 ml) at 0° (ice-bath) was added $BF_3 \cdot OEt_2$ (37.5 ml, 296.2 mmol). After stirring for 8 h at r.t. and workup, a brownish oil (44.0 g) was isolated. Purification by FC (pentane/Et_2O 2:1 → 1:1 → 1:2) gave **11** (16.3 g, 44%) as a crystalline solid. R_f 0.20 (Et_2O/pentane 2:1). M.p. 58–59°. $[\alpha]_D^{r.t.} = -2.45$ (c = 0.98, $CHCl_3$). IR ($CHCl_3$): 3035*w*, 2955*w*, 1755*s*, 1440*m*, 1120*m*, 1105*s*, 990*m*, 915*w*, 840*m*. ^{1}H-NMR (300 MHz): 3.82, 3.87 (2*s*, 2 MeO); 4.87, 4.98 (2*d*, J = 4.0, H–C(4), H–C(5)); 5.28 (*dd*, J = 0.8, 10.9, 1 vinyl. H); 5.78 (*dd*, J = 0.8, 17.6, 1 vinyl. H); 6.14 (*s*, H–C(2)); 6.72 (*dd*, J = 10.9, 17.6, 1 vinyl. H); 7.26–7.56 (*m*, 4 arom. H). ^{13}C-NMR (75 MHz): 52.84 (MeO); 77.20, 77.46 (C(4), C(5)); 106.56 (C(2)); 114.85 (CH_2); 126.21 (CH); 127.41 (CH); 134.73 (C); 136.38 (CH); 139.26 (C); 169.43, 170.06 (*C*OOMe). EI-MS: 291 (9, $[M - 1]^+$), 233 (29), 148 (89), 131 (100), 117 (57), 104 (50), 77 (22), 59 (17). Anal. calc. for $C_{15}H_{16}O_6$ (292.29): C 61.64, H 5.52; found: C 61.69, H 5.34.

Dimethyl (4R,5R)-2-(4-Ethenylphenyl)-2-methyl-1,3-dioxolane-4,5-dicarboxylate (**12**). Following the procedure described in [80], to a soln. of (*R,R*)-dimethyl tartrate (84.8 g, 476 mmol) and **9** (45.8 g, 238 mmol) in AcOEt (475 ml) at 0° (ice-bath) was added $BF_3 \cdot OEt_2$ (60 ml, 474 mmol). After stirring for 10 min at 0° and workup, a yellowish oil was isolated. Purification by FC (pentane/Et_2O 3:1) gave **12** (52.6 g, 72%) as a colorless oil. R_f 0.34 (pentane/Et_2O 3:1). $[\alpha]_D^{r.t.} = +21.8$ (c = 0.57, $CHCl_3$). IR ($CHCl_3$): 3010*m*, 2955*m*, 2850*w*, 1755*s*, 1630*m*, 1510*m*, 1440*s*, 1400*m*, 1375*m*, 1095*s*, 1015*m*, 990*m*, 915*m*, 845*s*. ^{1}H-NMR (300 MHz): 1.78 (*s*, Me); 3.54, 3.85 (2*s*, 2 MeO); 4.82, 4.88 (2*d*, J = 5.5, H–C(4), H–C(5)); 5.26 (*dd*, J = 0.9, 10.9, 1 vinyl. H); 5.75 (*dd*, J = 0.9, 17.6, 1 vinyl. H); 6.70 (*dd*, J = 10.9, 17.6, 1 vinyl. H); 7.37–7.47 (*m*, 4 arom. H). ^{13}C-NMR (75 MHz): 28.13 (Me); 52.41, 52.86 (MeO); 113.27 (C(2)); 114.37 (CH_2); 125.76 (CH); 125.92 (CH); 136.35 (CH); 137.77 (C); 141.07 (C); 169.33, 169.52 (*C*OOMe). EI-MS: 307 (1, $[M + 1]^+$), 306 (5), 292 (21), 291 (100), 247 (11), 203 (4), 132 (6), 131 (60), 129 (16), 103 (11), 77 (8), 59 (5), 43 (6). Anal. calc. for $C_{16}H_{18}O_6$ (306.31): C 62.74, H 5.92; found: C 62.73, H 5.79.

Dimethyl (4R,5R)-2-(4-Ethenylphenyl)-2-phenyl-1,3-dioxolane-4,5-dicarboxylate (**13**). Following the procedure described in [80], to a soln. of (*R,R*)-dimethyl tartrate (36.0 g, 202 mmol) and crude **10** (25.7 g, 101 mmol) in AcOEt (200 ml) at 0° (ice-bath) was added $BF_3 \cdot OEt_2$ (25 ml, 202 mmol). After stirring for 2 h at 0° and workup, a yellowish oil was isolated. Recrystallization from Et_2O/pentane gave pure **13** (23.7 g). Purification of the mother liquid by FC (pentane/Et_2O 3:1) gave additionally **13** (10.1 g, total yield 33.8 g, 91%) as a colorless solid. R_f 0.31 (pentane/Et_2O 3:1). M.p. 52.5–54.0°. $[\alpha]_D^{r.t.} = +63.8$ (c = 2.45, $CHCl_3$). IR ($CHCl_3$): 3050*m*, 1750*s*, 1630*w*, 1505*w*, 1450*m*, 1440*s*, 1400*m*, 1265*m*, 1105*s*, 1020*m*, 990*w*, 945*w*, 915*m*, 845*s*. ^{1}H-NMR (300 MHz): 3.69, 3.70 (2*s*, 2 MeO); 4.92 (*s*, H–C(4), H–C(5)); 5.25 (*dd*, J = 0.9, 10.9, 1 vinyl. H); 5.74 (*dd*, J = 0.9, 17.6, 1 vinyl. H); 6.69 (*dd*, J = 10.9, 17.6, 1 vinyl. H); 7.30–7.38, 7.46–7.55 (2*m*, 9 arom. H). ^{13}C-NMR (75 MHz): 52.64 (MeO); 113.24 (C(2)); 114.59 (CH_2); 125.92 (CH); 126.67 (CH); 126.96 (CH); 128.06 (CH); 128.77 (CH); 136.35 (CH); 138.03 (C); 139.81 (C); 140.29 (C); 169.13 (*C*OOMe). EI-MS: 369 (3, $[M + 1]^+$), 368 (13, M^+), 309 (14), 292 (17), 291 (100), 266 (5), 265 (39), 208 (5), 193 (9), 180 (28), 131 (44), 105 (26), 103 (10), 77 (16). Anal. calc. for $C_{21}H_{20}O_6$ (368.39): C 68.47, H 5.47; found: C 68.51, H 5.51.

4-(Dimethoxymethyl)benzyl Alcohol (**14**). Following the procedure described in [85], to a soln. of methyl 4-formylbenzoate (8.2 g, 50 mmol) and $HC(OMe)_3$ (5.5 ml, 50 mmol) in MeOH (10.1 ml, 250 mmol) at r.t. was added $[Rh(triphos)(MeCN)_3] \cdot OTf_3$ (5 mg). After stirring for 5 h at r.t., molecular-sieves (4 Å) powder (2.0 g) was added, filtrated over *Celite* and evaporated to give methyl 4-(dimethoxymethyl)benzoate (10.6 g, 99%) as a colorless oil. A soln. of the crude product (10.6 g) in Et_2O (50 ml) was added at 0° (ice-bath) dropwise to a suspension of $LiAlH_4$ (1.4 g, 36.8 mmol) in Et_2O (80 ml). After stirring for 1 h at r.t., the mixture was carefully hydrolyzed by addition of H_2O (1.4 ml), 20% NaOH (1.1 ml), and H_2O (4.9 ml), dried ($MgSO_4$), and evaporated to give **14** (9.0 g, 95%) as a colorless solid. M.p. 42.5–43.5° ([86]: 42–43°). ^{1}H-NMR (300 MHz): 1.71 (*t*, J = 6.0, OH); 3.33 (*s*, 2 MeO); 4.71 (*d*, J = 6.1, CH_2); 5.40 (*s*, $HC(OMe)_2$); 7.37–7.47 (*m*, 4 arom. H).

4-(Dimethoxymethyl)benzyl Benzoate (**15**). A cold soln. (ice-bath) of crude **14** (9.0 g, 49.5 mmol) in CH_2Cl_2 (100 ml) was treated with Et_3N (14.0 ml, 100 mmol) and PhCOCl (6.0 ml, 51.6 mmol). After stirring for 5 h at r.t., the suspension was filtered and evaporated. The resulting solid was dissolved in CH_2Cl_2, washed with 10% aq. $CuSO_4$, sat. aq. NaCl soln., dried ($MgSO_4$), and evaporated to give **15** (14.3 g, 99%) as a crystalline solid. M.p. 38.0–38.5°. IR ($CHCl_3$): 3010*w*, 2935*w*, 2830*w*, 1720*s*, 1450*m*, 1315*m*, 1270*s*, 1100*s*, 1055*s*, 980*w*. ^{1}H-NMR (300 MHz): 3.34 (*s*, 2 MeO); 5.38 (*s*, PhCH_2); 5.41 (*s*, $HC(OMe)_2$); 7.42–7.60, 8.07–8.10 (2*m*, 9 arom. H). ^{13}C-NMR

(75 MHz): 52.69 (Me); 66.35 (CH_2); 102.85 (CH); 126.98, 127.98, 128.34, 129.67 (CH); 130.09 (C); 133.00 (CH); 136.26, 138.18 (C); 166.36 (COOR). EI-MS: 285 (1, $[M-1]^+$), 255 (100), 165 (2), 149 (2), 134 (7), 119 (6), 105 (46), 91 (14), 77 (12). Anal. calc. for $C_{17}H_{18}O_4$ (286.33): C 71.31, H 6.34; found: C 71.25, H 6.29.

Dimethyl (4R,5R)-2-[4-(Benzyloxymethyl)phenyl]-1,3-dioxolane-4,5-dicarboxylate (**16**). Following the procedure described in [80], to a soln. of (*R,R*)-dimethyl tartrate (3.1 g, 17.5 mmol) and **15** (5.0 g, 17.5 mmol) in AcOEt (35 ml) at 0° (ice-bath) was added $BF_3 \cdot OEt_2$ (4.4 ml, 35.0 mmol). After stirring for 7 h at r.t. and workup, a yellowish oil was isolated. Purification by recrystallization from Et_2O/pentane gave **16** (5.2 g, 74%) as colorless crystals. M.p. 64–65°. $[\alpha]_D^{r.t.} = -6.4$ ($c = 1.03$, $CHCl_3$). IR ($CHCl_3$): 3010*m*, 2955*w*, 1755*s*, 1720*s*, 1440*m*, 1315*m*, 1275*s*, 1105*s*, 1070*m*, 1025*m*, 970*w*. ^{1}H-NMR (300 MHz): 3.83, 3.88 (2*s*, 2 MeO); 4.87, 4.99 (2*d*, $J = 4.0$, H–C(4), H–C(5)); 5.38 (*s*, PhCH_2); 6.17 (*s*, H–C(2)); 7.41–7.87, 8.05–8.09 (2*m*, 9 arom. H). ^{13}C-NMR (75 MHz): 52.86 (MeO); 66.25 (CH_2); 77.24, 77.46 (C(4), C(5)); 106.44 (C(2)); 127.48, 128.12, 128.41, 129.71 (CH); 130.07 (C); 133.08 (CH); 135.43, 137.96 (C); 166.32, 169.40, 170.01 (*C*OOMe). EI-MS: 399 (4, $[M-1]^+$), 341 (13), 295 (2), 278 (4), 256 (11), 239 (40), 119 (7), 105 (100), 91 (21), 77 (19), 59 (7). Anal. calc. for $C_{21}H_{20}O_8$ (400.39): C 63.00, H 5.03; found: C 62.96, H 5.11.

ent-**16**: Following the procedure described in [80], to a soln. of (*S,S*)-dimethyl tartrate (13.6 g, 76.4 mmol) and **15** (22.2 g, 76.4 mmol) in AcOEt (150 ml) at 0° (ice-bath) was added $BF_3 \cdot OEt_2$ (28.8 ml, 229.2 mmol). After stirring for 3 h at r.t. and workup, a yellowish oil was isolated. Purification by FC (pentane/Et_2O 2:1 → 1:1) and recrystallization from Et_2O/pentane gave *ent*-**16** (17.4 g, 57%) as colorless crystals. R_f 0.28 (pentane/Et_2O 2:1). M.p. 62.5–63°. $[\alpha]_D^{r.t.} = +6.5$ ($c = 1.08$, $CHCl_3$).

(4R,5R)-2-(4-Ethenylphenyl)-α,α,α′,α′-tetraphenyl-1,3-dioxolane-4,5-dimethanol (**18**). According to [80], **11** (21.0 g, 69.1 mmol) in THF (100 ml) was added to PhMgBr (293.6 mmol, prepared from PhBr (31.0 ml) and Mg (7.15 g)) in THF (200 ml). After stirring for 1.5 h at r.t. and workup, the crude product was purified by FC (CH_2Cl_2/pentane 9:1) to give **18** (29.9 g) as a yellowish solid. Further purification by FC (CH_2Cl_2/pentane 9:1) gave **18** (23.5 g, 63%) as a white powder. R_f 0.31 (CH_2Cl_2/pentane 9:1). M.p. 104–105°. $[\alpha]_D^{r.t.} = +63.2$ ($c = 0.98$, $CHCl_3$). IR ($CHCl_3$): 3565*m*, 3395*s* (br.), 3090*m*, 3060*m*, 3010*s*, 1630*w*, 1495*s*, 1450*s*, 1390*m*, 1170*m*, 1090*s*, 1015*s*, 840*s*. ^{1}H-NMR (400 MHz): 2.15, 3.26 (2*s*, 2 OH); 5.13 (*d*, $J = 5.0$, H–C(4) or H–C(5)); 5.17 (*s*, H–C(2)); 5.22 (*dd*, $J = 0.8$, 10.9, 1 vinyl. H); 5.31 (*d*, $J = 5.0$, H–C(4) or H–C(5)); 5.70 (*dd*, $J = 0.8$, 17.6, 1 vinyl. H); 6.65 (*dd*, $J = 10.9$, 17.6, 1 vinyl. H); 7.12–7.56 (*m*, 24 arom. H). ^{13}C-NMR (100 MHz): 78.51, 78.64 (C); 80.82, 81.58 (C(4), C(5)); 104.78 (C(2)); 114.58 (CH_2); 126.07, 126.87, 126.97, 127.05, 127.20, 127.26, 127.38, 127.51, 127.73, 127.87, 127.89, 128.17, 128.25 (CH); 136.34 (C); 136.46 (CH); 138.69, 143.03, 144.21, 144.32, 146.10 (C). EI-MS: 540 (< 1, M^+), 358 (1), 269 (2), 225 (2), 207 (20), 183 (33), 167 (19), 133 (24), 105 (100), 77 (47), 44 (40). Anal. calc. for $C_{37}H_{32}O_4$ (540.66): C 82.20, H 5.97; found: C 82.03, H 5.86.

(4R,5R)-2-(4-Ethenylphenyl)-α,α,α′,α′-tetra(naphthalen-1-yl)-1,3-dioxolane-4,5-dimethanol (**19**). According to [80], **11** (5.0 g, 17.2 mmol) in THF (50 ml) was added to (naphthalen-1-yl)magnesium bromide (72.7 mmol, prepared from 1-bromonaphthalene (10.2 ml) and Mg (1.86 g)) in THF (75 ml). After stirring for 2 h at r.t. and workup, the crude product was purified by FC (CH_2Cl_2/pentane 1:1) to give **19** (13.0 g) as a yellowish solid. Further purification by FC (CH_2Cl_2/pentane 1:1) gave **19** (8.45 g, 70%) as a white powder. R_f 0.34 (CH_2Cl_2/pentane 1:1). M.p. 200–210°. $[\alpha]_D^{r.t.} = +12.8$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 3575*s*, 3395*m* (br.), 3050*s*, 3005*s*, 1600*m*, 1510*s*, 1395*s*, 1300*m*, 1085*s*, 1015*s*, 915*m*, 895*m*, 840*m*. ^{1}H-NMR (200 MHz, (D_6)DMSO, 100°): 5.20 (*d*, $J = 10.8$, 1 vinyl. H); 5.67 (*d*, $J = 17.6$, 1 vinyl. H); 5.82–5.98 (*m*, H–C(2), H–C(4), H–C(5)); 6.61 (*dd*, $J = 10.8$, 17.6, 1 vinyl. H); 6.2–8.4 (br. *m*, 32 arom. H). FAB-MS (3-NOBA): 1480 (< 1, $2M^+$), 740 (2, M^+), 591 (6), 411 (25), 308 (35), 295 (26), 283 (57), 279 (32), 267 (100), 252 (15), 243 (24), 167 (15). Anal. calc. for $C_{53}H_{40}O_4$ (740.90): C 85.92, H 5.44; found: C 85.92, H 5.70.

(4R,5R)-2-(4-Ethenylphenyl)-α,α,α′,α′-tetra(naphthalen-2-yl)-1,3-dioxolane-4,5-dimethanol (**20**). According to [80], **11** (5.0 g, 17.2 mmol) in THF (50 ml) was added to (naphthalen-2-yl)magnesium bromide (72.7 mmol, prepared from 2-bromonaphthalene (15.1 g) and Mg (1.86 g)) in THF (75 ml). After stirring for 2 h at r.t. and workup, the crude product was purified by FC two times (CH_2Cl_2/pentane 3:2) to give **20** (10.3 g, 81%) as a white powder. R_f 0.25 (CH_2Cl_2/pentane 3:2). M.p. 165–170°. $[\alpha]_D^{r.t.} = +20.0$ ($c = 1.02$, $CHCl_3$). IR ($CHCl_3$): 3565*m*, 3395*m* (br.), 3060*m*, 3005*m*, 1630*w*, 1600*m*, 1505*m*, 1360*m*, 1270*m*, 1120*s*, 1095*s*, 1015*s*, 900*m*, 860*m*. ^{1}H-NMR (400 MHz): 2.74, 3.36 (2*s*, 2 OH); 5.21 (*dd*, $J = 0.8$, 10.9, 1 vinyl. H); 5.59 (*d*, $J = 4.2$, H–C(4) or H–C(5)); 5.68 (*dd*, $J = 0.8$, 17.6, 1 vinyl. H); 5.76 (*d*, $J = 4.2$, H–C(4) or H–C(5)); 5.89 (*s*, H–C(2)); 6.64 (*dd*, $J = 10.9$, 17.6, 1 vinyl. H); 6.80–6.96 (*m*, 4 arom. H); 7.23–7.29 (*m*, 4 arom. H); 7.35–7.56 (*m*, 12 arom. H); 7.65–7.94 (*m*, 8 arom. H); 8.06–8.29 (*m*, 4 arom. H). ^{13}C-NMR (100 MHz): 79.31, 80.30 (C); 81.38, 81.62 (C(4), C(5)); 105.58 (C(2)); 114.58 (CH_2); 124.56, 124.79, 124.87, 125.05, 125.92, 125.96, 126.04, 126.19, 126.22, 126.26, 126.36, 126.45, 126.55, 126.66, 127.07, 127.33, 127.36, 127.44, 127.47, 127.52, 127.65, 127.80, 127.90, 128.33, 128.37, 128.51, 128.58 (CH); 132.19, 132.33, 132.52, 132.60, 132.74, 132.78, 132.91 (C); 136.32 (CH); 136.96, 138.60, 140.53, 141.30, 141.65,

142.08 (C). FAB-MS (3-NOBA): 739 (2, $[M-1]^+$), 723 (2), 591 (4), 573 (2), 411 (16), 308 (20), 295 (28), 283 (60), 267 (100), 252 (9). Anal. calc. for $C_{53}H_{40}O_4$ (740.90): C 85.92, H 5.44; found: C 85.89, H 5.70.

(4R,5R)-2-(4-Ethenylphenyl)-2-methyl-α,α,α′,α′-tetraphenyl-1,3-dioxolane-4,5-dimethanol (**21**). According to [80], **12** (4.0 g, 13.0 mmol) in THF (20 ml) was added to PhMgBr (55.0 mmol, prepared from PhBr (5.8 ml) and Mg (1.35 g)) in THF (40 ml). After stirring for 3 h at 0° (ice-bath) and workup, the crude product was purified by FC (pentane/Et_2O 3:1) to give **21** (5.2 g, 72%) as a white powder. R_f 0.29 (pentane/Et_2O 3:1). M.p. 76–78°. $[\alpha]_D^{r.t.} = +83.9$ ($c = 0.83$, $CHCl_3$). IR ($CHCl_3$): 3545*s*, 3375 (br.), 3060*m*, 3010*s*, 1650*w*, 1630*w*, 1600*w*, 1495*s*, 1450*s*, 1400*w*, 1370*m*, 1180*m*, 1135*w*, 1110*w*, 1080*m*, 1045*m*, 1015*m*, 990*w*, 915*s*, 845*s*. ^{1}H-NMR (500 MHz): 1.32 (*s*, Me); 2.30, 2.47 (2*s*, 2 OH); 5.08, 5.17 (2*d*, $J = 5.6$, H–C(4), H–C(5)); 5.25 (*dd*, $J = 0.8$, 10.9, 1 vinyl. H); 5.74 (*dd*, $J = 0.8$, 17.7, 1 vinyl. H); 6.69 (*dd*, $J = 10.9$, 17.6, 1 vinyl. H); 7.06–7.40 (*m*, 22 arom. H); 7.52–7.55 (*m*, 2 arom. H). ^{13}C-NMR (125 MHz): 29.92 (Me); 78.44, 78.98 (C); 81.71, 83.25 (C(4), C(5)); 111.31 (C(2)); 114.25 (CH_2); 115.28, 120.74, 124.96, 126.38, 126.56, 126.83, 127.01, 127.03, 127.22, 127.25, 127.36, 127.48, 127.53, 127.65, 128.07, 128.11, 128.31, 129.64, 136.34 (CH); 137.27, 143.33, 143.44, 144.55, 145.05, 145.14 (C). FAB-MS (3-NOBA): 555 (2, M^+), 391 (12), 355 (8), 326 (11), 325 (39), 195 (15), 183 (43), 179 (23), 147 (90), 131 (15), 105 (100), 91 (12), 77 (28). Anal. calc. for $C_{38}H_{34}O_4$ (554.69): C 82.28, H 6.18; found: C 81.77, H 6.26.

(4R,5R)-2-(4-Ethenylphenyl)-2,α,α,α′,α′-pentaphenyl-1,3-dioxolane-4,5-dimethanol (**22**). According to [80], **13** (8.8 g, 24.0 mmol) in THF (40 ml) was added to PhMgBr (102.0 mmol, prepared from PhBr (10.7 ml) and Mg (2.49 g)) in THF (80 ml). After stirring for 2 h at 0° (ice-bath) and workup, the crude product was purified by FC (pentane/Et_2O 4:1) to give **22** (7.3 g, 49%) as a white powder. R_f 0.26 (pentane/Et_2O 4:1). M.p. 105–106°. $[\alpha]_D^{r.t.} = +177.8$ ($c = 0.85$, $CHCl_3$). IR ($CHCl_3$): 3550*s*, 3060*m*, 3005*m*, 1700*w*, 1630*m*, 1600*m*, 1495*s*, 1450*s*, 1400*m*, 1165*m*, 1105*s*, 945*m*, 915*m*, 845*s*, 615*s*. ^{1}H-NMR (400 MHz): 2.04, 2.09 (2*s*, 2 OH); 5.20 (*dd*, $J = 0.8$, 10.9, 1 vinyl. H); 5.53 (*s*, H–C(4), H–C(5)); 5.66 (*dd*, $J = 0.8$, 17.6, 1 vinyl. H); 6.61 (*dd*, $J = 10.9$, 17.6, 1 vinyl. H); 6.87–6.96 (*m*, 6 arom. H); 7.02–7.04 (*m*, 4 arom. H); 7.16–7.30 (*m*, 15 arom. H); 7.46–7.50 (*m*, 4 arom. H). ^{13}C-NMR (100 MHz): 79.50, 79.54 (C); 83.66, 83.69 (C(4), C(5)); 112.06 (C(2)); 114.35 (CH_2); 124.94, 125.19, 125.72, 126.42, 126.45, 126.78, 127.11, 127.15, 127.78, 127.99, 128.05, 128.56, 136.21 (CH); 137.20, 142.36, 144.02, 144.50, 145.74 (C). FAB-MS (3-NOBA): 617 (< 1, M^+), 387 (19), 210 (19), 209 (88), 195 (9), 183 (21), 179 (17), 178 (12), 167 (57), 165 (11), 152 (6), 131 (25), 105 (100), 91 (7), 77 (26). Anal. calc. for $C_{43}H_{36}O_4$ (616.76): C 83.74, H 5.88; found: C 83.75, H 6.13.

(4R,5R)-2-[4-(Hydroxymethyl)phenyl]-α,α,α′,α′-tetraphenyl-1,3-dioxolane-4,5-dimethanol (**23**). According to [80], **16** (19.0 g, 49.8 mmol) in THF (100 ml) was added to PhMgBr (350.0 mmol, prepared from PhBr (36.8 ml) and Mg (8.5 g)) in THF (250 ml). After stirring for 4 h at r.t. and workup, the crude product was purified by FC (pentane/Et_2O 1:1→1:2→1:3) to give **23** (23.5 g, 87%) as a white powder. R_f 0.29 (Et_2O/pentane 2:1). M.p. 128–132°. $[\alpha]_D^{r.t.} = +28.0$ ($c = 1.04$, $CHCl_3$). IR ($CHCl_3$): 3565*m*, 3405*w* (br.), 3010*s*, 2880*w*, 1600*w*, 1495*s*, 1450*s*, 1375*m*, 1170*m*, 1085*s*, 1015*s*, 890*m*. ^{1}H-NMR (300 MHz): 1.66 (*t*, $J = 5.8$, OH); 2.25, 3.36 (2*s*, 2 OH); 4.61 (*d*, $J = 5.8$, CH_2); 5.12 (*d*, $J = 5.0$, H–C(4) or H–C(5)); 5.16 (*s*, H–C(2)); 5.30 (*d*, $J = 5.0$, H–C(4) or H–C(5)); 7.13–7.54 (*m*, 24 arom. H). ^{13}C-NMR (75 MHz): 64.97 (CH_2); 78.51, 78.66 (C); 80.86, 81.62 (C(4), C(5)); 104.78 (C(2)); 126.76, 126.89, 127.05, 127.22, 127.38, 127.52, 127.74, 127.90, 128.19 (CH); 136.50, 142.12, 143.05, 144.25, 144.34, 146.09 (C). EI-MS: 544 (< 1, M^+), 360 (1), 344 (12), 208 (21), 207 (21), 183 (44), 137 (28), 120 (21), 105 (100), 84 (48), 49 (65). Anal. calc. for $C_{36}H_{32}O_5$ (544.65): C 79.39, H 5.92; found: C 79.16, H 6.00.

ent-**23**: According to [80], *ent*-**16** (16.4 g, 41.0 mmol) in THF (100 ml) was added to PhMgBr (287.0 mmol, prepared from PhBr (30.0 ml) and Mg (7.0 g)) in THF (200 ml). After workup, the crude product was purified by FC (pentane/Et_2O 1:1→1:2→1:3) to give *ent*-**23** (18.4 g, 82%) as a white powder. R_f 0.16 (pentane/Et_2O 1:1). M.p. 118–122°. $[\alpha]_D^{r.t.} = -29.8$ ($c = 1.1$, $CHCl_3$).

(4R,5R)-α′,α′-Bis(4-ethenylphenyl)-2,2-dimethyl-α,α-diphenyl-1,3-dioxolane-4,5-dimethanol (**24**). According to [80], **17** [15] (7.8 g, 22.7 mmol) in THF (15 ml) was added to (4-vinylphenyl)magnesium chloride (79.5 mmol, prepared from 4-chlorostyrene (10.7 g) and Mg (3.86 g)) in THF (20 ml). After stirring for 18 h at r.t. and workup, the crude product was purified by FC (pentane/Et_2O 4:1) to give **24** (9.8 g, 83%) as a white powder. R_f 0.38 (pentane/Et_2O 4:1). M.p. 158–162°. $[\alpha]_D^{r.t.} = -61.0$ ($c = 0.5$, $CHCl_3$). IR ($CHCl_3$): 3590*s*, 3370*s*, 2930*m*, 1730*s*, 1630*s*, 1560*m*, 1490*m*, 1455*s*, 1400*m*, 1370*s*, 1170*s*, 1080*s*, 1010*m*, 910*s*, 880*s*. ^{1}H-NMR (400 MHz): 1.03, 1.08 (2*s*, 2 Me); 3.91, 4.04 (2*s*, 2 OH); 4.56, 4.60 (2*d*, $J = 7.8$, H–C(4), H–C(5)); 5.20, 5.25 (2*dd*, $J = 0.9$, 10.9, 2 vinyl. H); 5.68, 5.77 (2*dd*, $J = 0.9$, 17.6, 2 vinyl. H); 6.65, 6.73 (2*dd*, $J = 10.9$, 17.6, 2 vinyl. H); 7.21–7.53 (*m*, 18 arom. H). ^{13}C-NMR (100 MHz): 27.13, 27.28 (Me); 77.89, 78.25 (C); 80.96, 81.06 (C(4), C(5)); 109.56 (C(2)); 113.85, 114.12 (CH_2); 125.22, 125.95, 127.28, 127.32, 127.59, 127.74, 128.16, 128.57, 136.36, 136.44 (CH); 136.58, 136.79, 142.38, 142.69, 145.27, 145.76 (C). EI-MS: 518 (< 1, M^+), 285 (3), 260 (2), 235 (30), 183 (25), 131 (56), 105 (100), 91 (59), 84 (38), 77 (42), 49 (59). Anal. calc. for $C_{35}H_{34}O_4$ (518.65): C 81.05, H 6.61; found: C 81.05, H 6.65.

(4R,5R)-2-{4-[(4-Ethenylbenzyloxy)methyl]phenyl}-α,α,α',α'-tetraphenyl-1,3-dioxolane-4,5-dimethanol (**25**). A soln. of **23** (2.7 g, 5.0 mmol) in DMF (25 ml) was treated with NaH (390 mg, 16.25 mmol). After stirring for 4 h, to the brownish mixture was added 4-vinylbenzyl chloride[33]) (800 mg, 5.25 mmol) in DMF (10 ml). After stirring for 18 h, the orange mixture was hydrolyzed with H_2O (*ca.* 3 ml) and evaporated (h.v.). the resulting brown oil was dissolved in CH_2Cl_2, washed with H_2O (2×) and sat. aq. NaCl soln., dried ($MgSO_4$), and evaporated. Purification by FC (CH_2Cl_2) gave **25** (2.1 g, 64%) as a white powder. R_f 0.40 (CH_2Cl_2). M.p. 78–81°. $[\alpha]_D^{r.t.}$ = +36.7 (c = 1.0, $CHCl_3$). IR ($CHCl_3$): 3565*m*, 3400*w* (br.), 3060*m*, 3010*s*, 2860*m*, 1495*s*, 1445*s*, 1360*m*, 1085*s*, 1020*s*, 915*m*, 830*m*. ^{1}H-NMR (300 MHz): 2.15, 3.31 (2*s*, 2 OH); 4.48, 4.49 (2*s*, 2 PhCH_2); 5.13 (*d*, J = 5.0, H–C(4) or H–C(5)); 5.16 (*s*, H–C(2)); 5.23 (*dd*, J = 0.9, 10.9, 1 vinyl. H); 5.31 (*d*, J = 5.0, H–C(4) or H–C(5)); 5.74 (*dd*, J = 0.9, 17.6, 1 vinyl. H); 6.70 (*dd*, J = 10.9, 17.6, 1 vinyl. H); 7.15–7.55 (*m*, 28 arom. H). ^{13}C-NMR (75 MHz): 71.57, 71.73 (CH_2); 78.50, 78.62 (C); 80.80, 81.57 (C(4), C(5)); 104.81 (C(2)); 113.80 (CH_2); 126.25, 126.87, 127.05, 127.25, 127.28, 127.53, 127.74, 127.87, 128.16, 136.42 (CH); 136.54, 137.03, 137.74, 139.58, 143.02, 144.18, 144.34, 146.11 (C). FAB-MS (3-NOBA): 660 (5, M^+), 431 (20), 391 (19), 344 (7), 307 (6), 253 (43), 209 (11), 207 (11), 195 (46), 183 (58), 167 (92), 154 (33), 136 (29), 117 (76), 105 (100). Anal. calc. for $C_{45}H_{40}O_5$ (660.81): C 81.79, H 6.10; found: C 81.75, H 6.30.

(4R,5R)-α,α,α',α'-Tetraphenyl-2-{4-[(prop-2-enoyloxy)methyl]phenyl}-1,3-dioxolane-4,5-dimethanol (**26**). A cold soln. (ice-bath) of **23** (8.6 g, 15.8 mmol) in CH_2Cl_2 (150 ml) was treated with Et_3N (2.65 ml, 19.0 mmol) and acryloyl chloride (1.3 ml, 15.8 mmol) and stirred for 1 h at r.t. The mixture was diluted with H_2O, extracted with CH_2Cl_2, dried ($MgSO_4$), and evaporated. Purification by FC (pentane/Et_2O 1:1) gave **26** (8.6 g, 91%) as a white powder. R_f 0.36 (pentane/Et_2O 1:1). M.p. 90–95°. $[\alpha]_D^{r.t.}$ = +32.2 (c = 1.01, $CHCl_3$). IR ($CHCl_3$): 3565*m*, 3395*m* (br.), 3090*w*, 3010*m*, 1725*s*, 1635*w*, 1495*s*, 1405*s*, 1295*m*, 1275*m*, 1180*s*, 1090*s*, 985*s*, 890*m*. ^{1}H-NMR (400 MHz): 2.19, 3.27 (2*s*, 2 OH); 5.12 (*d*, J = 5.0, H–C(4) or H–C(5)); 5.13 (*s*, PhCH_2); 5.16 (*s*, H–C(2)); 5.31 (*d*, J = 5.0, H–C(4) or H–C(5)); 5.82 (*dd*, J = 1.4, 10.4, 1 vinyl. H); 6.12 (*dd*, J = 10.4, 17.4, 1 vinyl. H); 6.40 (*dd*, J = 1.4, 17.4, 1 vinyl. H); 7.13–7.53 (*m*, 24 arom. H). ^{13}C-NMR (100 MHz): 65.89 (CH_2); 78.49, 78.61 (C); 80.84, 81.61 (C(4), C(5)); 104.62 (C(2)); 126.88, 127.04, 127.23, 127.29, 127.40, 127.53, 127.73, 127.89, 128.13, 128.20, 128.25 (CH); 131.17 (CH_2); 137.06, 137.10, 142.99, 144.22, 144.24, 146.09 (C); 165.09 (COOR). EI-MS: 598 (< 1, M^+), 527 (< 1), 369 (1), 344 (31), 225 (10), 208 (30), 183 (67), 167 (11), 120 (38), 105 (100), 77 (31), 55 (6). Anal. calc. for $C_{39}H_{34}O_6$ (598.70): C 78.24, H 5.72; found: C 78.08, H 5.89.

3. *Preparation of the Dendrimer-Bound TADDOLs* **28–31**. *(4R,5R)-2-[4-(Bromomethyl)phenyl]-α,α,α',α'-tetraphenyl-1,3-dioxolane-4,5-dimethanol* (**27**). A soln. of **23** (6.3 g, 9.8 mmol) in THF (50 ml) was treated with Ph_3P (3.2 g, 12.25 mmol) and CBr_4 (4.1 g, 12.25 mmol) and stirred at r.t. After 30 min, more Ph_3P (1.6 g) and CBr_4 (2.0 g) were added and stirred for another 30 min. For workup, the mixture was diluted with H_2O, extracted with CH_2Cl_2, dried ($MgSO_4$), and evaporated. Purification by FC (CH_2Cl_2) gave **27** (5.7 g, 95%) as a white powder. R_f 0.40 (CH_2Cl_2). M.p. 105-108°. $[\alpha]_D^{r.t.}$ = +36.0 (c = 1.0, $CHCl_3$). IR ($CHCl_3$): 3565*m*, 3410*m* (br.), 3005*m*, 1495*m*, 1450*s*, 1395*w*, 1170*w*, 1085*s*, 1020*s*, 890*m*. ^{1}H-NMR (300 MHz): 2.15, 2.92 (2*s*, 2 OH); 4.42 (*s*, PhCH_2); 5.12 (*d*, J = 5.0, H–C(4) or H–C(5)); 5.13 (*s*, H–C(2)); 5.31 (*d*, J = 5.0, H–C(4) or H–C(5)); 7.12–7.53 (*m*, 24 arom. H). ^{13}C-NMR (75 MHz): 32.89 (CH_2); 78.50, 78.63 (C); 80.86, 81.61 (C(4), C(5)); 104.52 (C(2)); 126.89, 127.05, 127.28, 127.44, 127.57, 127.77, 127.91, 128.18, 128.28, 128.97 (CH); 137.24, 138.94, 142.98, 144.21, 146.08 (C). EI-MS: 527 (< 1, $[M - 80]^+$), 372 (< 1), 344 (2), 269 (1), 242 (1), 208 (17), 207 (17), 183 (38), 167 (17), 120 (18), 105 (100), 91 (16), 77 (38). Anal. calc. for $C_{36}H_{31}BrO_4$ (607.54): C 71.17, H 5.14; found: C 70.94, H 5.22.

Tris{{4-{(4R,5R)-4,5-bis[(hydroxy)(diphenyl)methyl]-1,3-dioxolan-2-yl}phenyl}methyl} Benzene-1,3,5-tricarboxylate (**28**). A soln. of **23** (1.9 g, 3.5 mmol) in CH_2Cl_2 (25 ml) was treated with benzene-1,3,5-tricarbonyl trichloride (266 mg, 1.0 mmol) and pyridine (325 µl, 4.0 mmol) and stirred for 2 d at r.t. For workup, the soln. was washed with H_2O, and the aq. phase extracted with CH_2Cl_2. The combined org. phases were dried ($MgSO_4$) and evaporated. Purification by FC (CH_2Cl_2/Et_2O 20:1) gave **28** (941 mg, 51%) and **23** (531 mg) as white powders. R_f 0.27 (CH_2Cl_2/Et_2O 20:1). M.p. 175–185°. $[\alpha]_D^{r.t.}$ = +62.2 (c = 1.01, $CHCl_3$). IR ($CHCl_3$): 3565*m* (br.), 3410*w* (br.), 3060*m*, 3005*m*, 1725*s*, 1600*w*, 1495*m*, 1445*s*, 1370*m*, 1330*w*, 1090*s*, 1000*s*, 910*m*. ^{1}H-NMR (400 MHz): 2.18, 3.22 (2*s*, 6 OH); 5.14 (*d*, J = 5.0, 3 H–C(4) or H–C(5)); 5.18 (*s*, 3 H–C(2)); 5.31 (*d*, J = 5.0, 3 H–C(4) or H–C(5)); 5.33 (*s*, 3 PhCH_2); 7.12–7.52 (*m*, 72 arom. H); 8.80 (*s*, 3 arom. H). ^{13}C-NMR (100 MHz): 66.95 (CH_2); 78.52, 78.65 (C); 80.88, 81.63 (C(4), C(5)); 104.61 (C(2)); 126.89, 127.04, 127.15, 127.25, 127.30, 127.41, 127.55, 127.74, 127.89, 127.92, 128.11, 128.17, 128.19, 128.27, 128.37 (CH); 131.19 (C); 134.83 (CH); 136.64, 137.36, 143.01, 144.21, 144.25, 146.08 (C); 164.63 (COOR). MALDI-TOF-MS (CCA): 1812.7 (100, $[M + Na]^+$), 1828.4 (35, $[M + K]^+$).

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[33]) Prepared by chloromethylation of $PhCH_2CH_2Br$ with formaldehyde dimethyl acetal and $SOCl_2$ [87], separation of the *ortho*-isomer by recrystallization from pentane and subsequent elimination with *t*-BuONa [88].

Tris{(1R)-3-{4-{(4R,5R)-4,5-bis[(hydroxy)(diphenyl)methyl]-1,3-dioxolan-2-yl}phenylmethoxy}-1-methyl-3-oxopropyl} Benzene-1,3,5-tricarboxylate (**29**). A soln. of tris[(1*R*)-2-carboxy-1-methylethyl] 1,3,5-benzenetricarboxylate [16] (515 mg, 1.1 mmol) in CH_2Cl_2 (35 ml) was treated with oxalyl chloride (425 µl, 4.95 mmol) and stirred at r.t. After 8 h, the solvent was evaporated (h.v.) and the resulting residue dried overnight under h.v. The viscous oil (acid chloride) was dissolved in CH_2Cl_2 (20 ml), and **23** (2.5 g, 4.5 mmol) was added. At −75°, the soln. was treated with pyridine (320 µl, 4.0 mmol) and slowly warmed to r.t. For workup, the mixture was hydrolyzed with aq. 1M HCl soln. (25 ml), extracted with CH_2Cl_2, dried ($MgSO_4$), and evaporated. Purification by FC (CH_2Cl_2/AcOEt 15:1) gave **23** (1.0 g) and **29**·1 toluene (1.24 g, 67%) as a white powder. R_f 0.45 (CH_2Cl_2/AcOEt 15:1). M.p. 117–130° (**29**·1 toluene). $[\alpha]_D^{r.t.} = +17.5$ (*c* = 1.14 (**29**·1 toluene), toluene). IR ($CHCl_3$): 3565*m* (br.), 3060*w*, 3005*m*, 1735*s*, 1495*s*, 1450*s*, 1385*m*, 1300*m*, 1100*m*, 1055*s*, 1005*m*, 890*m*. ^{1}H-NMR (400 MHz): 1.39 (*d*, *J* = 6.3, 3 Me); 2.30 (*s*, 3 OH); 2.61 (*dd*, *J* = 5.9, 15.7, 3 H–C(2′)); 2.80 (*dd*, *J* = 7.3, 15.7, 3 H–C(2′)); 3.19 (*s*, 3 OH); 4.98–5.04 (*m*, 3 PhCH_2); 5.13 (*d*, *J* = 4.9, 3 H–C(4) or H–C(5)); 5.22 (*s*, 3 H–C(2)); 5.30 (*d*, *J* = 4.9, 3 H–C(4) or H–C(5)); 5.49–5.57 (*m*, 3 H–C(3′)); 7.11–7.51 (*m*, 72 arom. H); 8.73 (*s*, 3 arom. H). ^{13}C-NMR (100 MHz): 19.98 (Me); 40.68 (CH_2); 66.17 (CH_2); 68.83 (C(3′)); 78.50, 78.76 (C); 78.87, 81.58 (C(4), C(5)); 104.65 (C(2)); 125.30, 126.82, 126.99, 127.20, 127.22, 127.33, 127.50, 127.72, 127.85, 127.90, 128.15, 128.24, 129.04 (CH); 131.30 (C); 134.57 (CH); 136.71, 137.21, 143.22, 144.17, 144.32, 145.91 (C); 164.09, 169.81 (*C*OOR). MALDI-TOF-MS (CCA): 2068.6 (100, $[M + Na - 2\,H]^+$), 2085.6 (55, $[M + K - H]^+$). Anal. calc. for $C_{129}H_{114}O_{24}\cdot C_7H_8$ (2140.5): C 76.32, H 5.75; found: C 75.83, H 5.99.

Ethane-1,1,1-triyltris{[(4,1-phenyleneoxy)methylene]-4,1-phenylene-2-[(4R,5R)-α,α,α′,α′-tetraphenyl-1,3-dioxolane-4,5-dimethanol]} (**30**). According to [89], a soln. of **27** (4.79 g, 7.0 mmol), 1,1,1-tris(4-hydroxyphenyl)ethane (0.65 g, 2.1 mmol), 18-crown-6 (0.2 g), and K_2CO_3 (0.97 g, 7.0 mmol) in acetone (75 ml) was heated to reflux. After 24 h, the mixture was filtered and evaporated. The resulting solid was dissolved in CH_2Cl_2 and washed with H_2O and sat. aq. NaCl soln., dried ($MgSO_4$), and evaporated. Purification by FC (first pentane/Et_2O 1:1, then CH_2Cl_2/AcOEt 25:1) gave **30** (3.6 g, 91%) as an amorphous solid. Several cycles of dissolving in toluene and evaporating of the solvent gave the toluene-clathrate **30**·2 toluene. R_f 0.40 (CH_2Cl_2/AcOEt 25:1). M.p. 160–170° (**30**·2 toluene). $[\alpha]_D^{r.t.} = +28.5$ (*c* = 1.0 (**30**·2 toluene), toluene). IR ($CHCl_3$): 3565*m*, 3400*m* (br.), 3060*m*, 3005*m*, 1605*m*, 1505*s*, 1495*s*, 1445*s*, 1375*m*, 1300*m*, 1175*s*, 1085*s*, 1020*s*, 890*m*. ^{1}H-NMR (400 MHz): 2.06 (*s*, 3 OH); 2.11 (*s*, Me); 3.23 (*s*, 3 OH); 4.96 (*s*, 3 PhCH_2); 5.13 (*d*, *J* = 5.0, 3 H–C(4) or H–C(5)); 5.18 (*s*, 3 H–C(2)); 5.31 (*d*, *J* = 5.0, 3 H–C(4) or H–C(5)); 6.77–6.80 (*m*, 6 arom. H); 6.93–6.98 (*m*, 6 arom. H); 7.04–7.59 (*m*, 72 arom. H). ^{13}C-NMR (100 MHz): 30.80 (Me); 50.63 (C); 69.53 (CH_2); 78.51, 78.63 (C); 80.84, 81.60 (C(4), C(5)); 104.75 (C(2)); 113.94, 125.30, 126.80, 126.86, 126.94, 127.02, 127.04, 127.22, 127.28, 127.35, 127.39, 127.52, 127.75, 127.86, 127.90, 128.08, 128.17, 128.23, 128.26, 129.04, 129.62, 129.77 (CH); 136.72, 138.46, 142.05, 143.01, 144.19, 144.31, 146.09, 156.68 (C). MALDI-TOF-MS (CCA): 1906.9 (100, $[M + Na - 2\,H]^+$), 1924.8 (30, $[M + K]^+$). Anal. calc. for $C_{128}H_{108}O_{15}\cdot 2\,C_7H_8$ (2070.53): C 82.37, H 6.04; found: C 82.31, H 6.10.

Ethane-1,1,1-triyltris{[(4,1-phenyleneoxy)methylene]benzene-5,1,3-triylbis{(oxymethylene)-4,1-phenylene-2-[(4R,5R)-α,α,α′,α′-tetraphenyl-1,3-dioxolane-4,5-dimethanol]}} (**31**). *Preparation of the Branches.* According to [89], a soln. of **27** (6.5 g, 10.0 mmol), 5-(hydroxymethyl)benzene-1,3-diol (560 mg, 4.0 mmol), 18-crown-6 (210 mg), and K_2CO_3 (1.4 g, 10.0 mmol) in acetone (40 ml) was heated to reflux. After 24 h, the mixture was filtered and evaporated. The resulting solid was dissolved in CH_2Cl_2 and washed with H_2O and sat. aq. NaCl soln., dried ($MgSO_4$), and evaporated. Purification by FC (pentane/AcOEt 1:1) gave *Branch-OH* (4.1 g, 86%) as an amorphous solid (formed a clathrate with AcOEt). R_f 0.28 (pentane/AcOEt 1:1). ^{1}H-NMR (400 MHz): 1.55, 2.25, 3.30 (3*s*, 5 OH); 4.55 (*s*, PhCH_2); 4.96 (*s*, 2 PhCH_2); 5.13 (*d*, *J* = 5.0, 2 H–C(4) or H–C(5)); 5.18 (*s*, 2 H–C(2)); 5.30 (*d*, *J* = 5.0, 2 H–C(4) or H–C(5)); 6.43–6.45 (*m*, 1 arom. H); 6.52–6.54 (*m*, 2 arom. H); 7.07–7.55 (*m*, 48 arom. H). ^{13}C-NMR (100 MHz): 65.20, 69.62 (CH_2); 78.49, 78.63 (C); 80.84, 81.62 (C(4), C(5)); 101.36 (CH); 104.71 (C(2)); 105.70, 126.87, 126.95, 127.05, 127.22, 127.27, 127.34, 127.39, 127.52, 127.74, 127.87, 127.90, 128.17, 128.25 (CH); 136.79, 138.11, 143.03, 143.44, 144.21, 159.99 (C).

A soln. of *Branch-OH* (3.63 g, 2.8 mmol) in THF (20 ml) was treated with Ph_3P (915 mg, 3.5 mmol) and CBr_4 (1.15 g, 3.5 mmol) and stirred at r.t. After 45 min, more Ph_3P (230 mg) and CBr_4 (290 mg) were added. For workup, the mixture was diluted with H_2O, extracted with CH_2Cl_2, dried ($MgSO_4$), and evaporated. Purification by FC (CH_2Cl_2, then CH_2Cl_2/AcOEt 100:1) gave *Branch-Br* (2.75 g, 73%) as a white powder (1:1 clathrate with AcOEt). R_f 0.37 (CH_2Cl_2/AcOEt 50:1). ^{1}H-NMR (300 MHz): 2.11, 3.22 (2*s*, 4 OH); 4.38 (*s*, PhCH_2); 4.97 (*s*, 2 PhCH_2); 5.14 (*d*, *J* = 5.0, 2 H–C(4) or H–C(5)); 5.18 (*s*, 2 H–C(2)); 5.33 (*d*, *J* = 5.0, 2 H–C(4) or H–C(5)); 6.42–6.48 (*m*, 1 arom. H); 6.53–6.60 (*m*, 2 arom. H); 7.10–7.58 (*m*, 48 arom. H).

According to [89], a soln. of *Branch-Br* (2.8 g, 1.77 mmol), 1,1,1-tris(4-hydroxyphenyl)ethane (136 mg, 0.44 mmol), 18-crown-6 (25 mg), and K_2CO_3 (250 mg, 1.77 mmol) in acetone (10 ml) was heated to reflux. After 24 h, the mixture was filtered and evaporated. The resulting solid was dissolved in CH_2Cl_2 and washed with H_2O

and sat. aq. NaCl soln., dried ($MgSO_4$), and evaporated. Purification by FC (CH_2Cl_2/AcOEt 1:1) gave **31** (2.27 g, clathrate with AcOEt) as a white powder. Further purification by FC (100 g SiO_2, first 600 ml of Et_2O/pentane 3:1, then CH_2Cl_2/AcOEt 23:1) and several cycles of dissolving in toluene and evaporating of the solvent gave **31**·4 toluene (1.49 g, 82%) as a white powder. R_f 0.14 (CH_2Cl_2/AcOEt 25:1). M.p. 180–190° (**31**·4 toluene). $[\alpha]_D^{r.t.} = +25.1$ ($c = 0.98$ (**31**·4 toluene), toluene). IR ($CHCl_3$): 3565*m*, 3400*m* (br.), 3060*w*, 3005*m*, 2925*m*, 1600*s*, 1495*s*, 1450*s*, 1375*m*, 1295*w*, 1155*s*, 1085*s*, 1020*s*, 890*w*. ^{1}H-NMR (400 MHz): 2.08 (*s*, Me); 2.16, 3.24 (2*s*, 12 OH); 4.90 (br. *s*, 3 PhCH_2); 4.95 (br. *s*, 6 PhCH_2); 5.13 (*d*, $J = 5.1$, 6 H–C(4) or H–C(5)); 5.17 (*s*, 6 H–C(2)); 5.30 (*d*, $J = 5.1$, 6 H–C(4) or H–C(5)); 6.41–6.46, 6.61–6.98 (2*m*, 20 arom. H); 7.07–7.58 (*m*, 145 arom. H). ^{13}C-NMR (100 MHz): 30.85 (Me); 50.67 (C); 69.68, 69.89 (CH_2); 78.50, 78.64 (C); 80.84, 81.61 (C(4), C(5)); 101.56 (CH); 104.72 (C(2)); 106.43, 113.97, 125.30, 126.81, 126.86, 126.94, 127.04, 127.22, 127.27, 127.33, 127.38, 127.52, 127.74, 127.85, 127.90, 128.16, 128.23, 128.25, 128.43, 129.04, 129.65, 129.75, 129.85, 129.93 (CH); 136.81, 137.87, 138.04, 139.57, 142.08, 143.02, 144.20, 144.26, 146.06, 147.41, 147.72, 156.78, 159.99 (C). MALDI-TOF-MS (CCA): 3855.4 (100, $[M + Na]^+$), 3869.2 (80, $[M + K - H]^+$). Anal. calc. for $C_{257}H_{216}O_{33}$·4.5 C_7H_8 (4229.14): C 81.51, H 6.01; found: C 81.24, H 6.26.

4. *Functionalization of a* Merrifield *Resin (Chloromethylated Polystyrene): Polymers* **32** *of Type I.* A cold soln. (ice-bath) of **23** (4.5 g, 8.0 mmol) in DMF (50 ml) was treated with NaH (600 mg, 25.0 mmol). After stirring for 3 h at r.t., to the brown mixture was added 5.7 g of *Merrifield* resin (0.7 mmol Cl/g, 4.0 mmol, DF *ca.* 0.08). The resulting suspension was stirred for 48 h at r.t. under Ar. The polymer was filtered (glass filter *G2*) and washed with THF (50 ml), MeOH (50 ml), H_2O (100 ml), THF/H_2O 1:1 (50 ml), THF (100 ml), MeOH (100 ml), and pentane/Et_2O (50 ml). After drying (h.v., 40–50°) 6.85 g of polymer **32** (56% conversion, 0.33 mmol TADDOL/g, DF *ca.* 0.04) was obtained.

Gel-phase ^{13}*C-NMR* [90]. In an NMR tube (ID 5 mm), polymer **32** was swelled in $CDCl_3$. The spectra was measured with a *Varian-Gemini 300* (75 MHz) at r.t. (see *Scheme 2*, AT 0.8, PW 12.0, D1 1, NT 11264, LB 2): 71.3 (CH_2Ph); 78.3 (CPh_2OH); 80.8, 81.6 (C(4), C(5)); 104.7 (C(2)).

In analogy, *ent*-**23** (4.5 g, 8.0 mmol) in DMF (50 ml) was treated with NaH (600 mg, 25.0 mmol) and 2.35 g of *Merrifield* resin (4.0 mmol, 1.7 mmol Cl/g, DF *ca.* 0.19). Workup after 48 h at 50–60° gave 2.8 g of *ent*-**32** (22% conversion, 0.32 mmol TADDOL/g, DF *ca.* 0.04).

5. *Suspension Copolymerization of the TADDOLs* **18–22** *and* **24–26**: *Polymers* **33–40** *of Type II–V. General Procedure for the Copolymerization (GP I).* A soln. of the TADDOL (*n* mmol, $n = 4$–16 mmol), styrene[34]) ($96 - n$ mmol), divinylbenzene[34]) (8.3 g, 32 mmol, as a 50% soln. of DVB in ethylinylbenzene), and AIBN[35]) (510 mg) in benzene (48 ml) and THF (15 ml) was added to a well stirred soln. of poly(vinyl alcohol) (0.8 g, degree of polymerization 100000, 86–89% hydrolyzed) in H_2O (200 ml) – which was prepared by violent stirring in warm water (40–50°) and filtering off of the unsoluble parts – in a three-necked flask, equipped with a thermometer, condenser, and an overhead stirrer (see [19]) under Ar. After stirring for 1 h at 0° (ice-bath) to homogenize the suspension, the apparatus was placed into a heat-bath (prewarmed on 60°), then the temp. was raised to 90°, and the white suspension was stirred for 44 h at that temp. For workup, the mixture was filtered through a glass filter (*G2*) and the resulting polymer beads were washed with hot H_2O (*ca.* 1 l), MeOH/H_2O 1:1 (200 ml), MeOH (200 ml), THF (2 × 200 ml), MeOH (200 ml), and pentane (200 ml), then collected and dried (h.v., 40–50°) to give the polymer in almost quantitative yield. Sieving the polymer beads through a sieve (mesh width: 1000, 800, 630, 500, 400, 250, 160, 100 μm) gave fractions of uniform particle size (see *Figs. 1* and *2*).

According to *GP I*, the TADDOLs **18–22**, **25** and **26** were copolymerized with styrene and DVB to give the polymers **33–39** (see *Scheme 3*). TADDOL **24** was polymerized with styrene to give **40** (polymer of Type V). The degree of functionalization (DF) is calculated from the percentage of the TADDOL an from the total amount monomers (% mol/mol). The loading is calculated from the portion of TADDOL (in mmol) from the amount of polymer (in g).

Detailed Example for the Preparation of the Polymer-Bound TADDOL **33c**. According to *GP I*, in a 500-ml flask a soln. of TADDOL **18** (2.22 g, 4.0 mmol), styrene (9.6 g, 92 mmol), DVB (8.3 g, 32 mmol DVB + 32 mmol ethylvinylbenzene), and AIBN (510 mg) in benzene (48 ml) and THF (15 ml) was suspended in soln. of poly(vinyl alcohol) (0.8 g) in H_2O (200 ml). After 44 h at 90°, the polymer beads were filtered, washed and dried (h.v., 50°) to give **33c** (19.4 g, 96%) as fine transparent particles: Degree of cross-linking: 20%, DF 0.025, Loading 0.20 mmol TADDOL/g. Anal. calc. for $\{(C_8H_8)_{0.575}\cdot(C_{10}H_{10})_{0.2}\cdot(C_{10}H_{12})_{0.2}\cdot(C_{37}H_{32}O_4)_{0.025}\}_n$ $[(C_{381}H_{392}O_4)_n, n\cdot(5035.7)]$: C 90.88, H 7.85; found: C 90.96, H 8.08.

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[34]) To remove the stabilizer, it was washed twice with 1% aq. NaOH and three times with H_2O.

[35]) AIBN was recrystallized from MeOH.

6. *Use of the Polymer-bound TADDOLs. Ti-TADDOLate-Catalyzed Addition of Et_2Zn to Benzaldehyde. (S)-1-Phenylpropan-1-ol* (**41**) (*GP II*). According to [44], the calculated amount of polymer-bound TADDOL (0.45 mmol) was suspended in toluene (10 ml) and stirred for 30 min, then the solvent was stripped off under h.v. at r.t. to remove traces of H_2O. The polymer was suspended again in toluene (15 ml) and $Ti(OCHMe_2)_4$ (135 µl, 0.45 mmol) was added and stirred for *ca.* 16 h. The Me_2CHOH liberated by ligand exchange was removed with the solvent under h.v. at r.t., and the polymer thus obtained was dried under h.v. at r.t. for 3–4 h. Toluene (15 ml) was added and the suspension was cooled to *ca.* −30°. Successively PhCHO (230 µl, 2.25 mmol), $Ti(OCHMe_2)_4$ (800 µl, 2.7 mmol), and Et_2Zn soln. (2.0 ml, 4.0 mmol, 2M in toluene) were added, and the suspension stirred for *ca.* 16 h at *ca.* −30°. For workup, 2M aq. HCl soln. was added, 30 min stirred at r.t., and filtered (glass filter *G2*). The polymer was washed with H_2O (50 ml), THF (10 ml), and Et_2O (50 ml). The phases were separated, the aq. layer extracted with Et_2O (2 × 50 ml), and the combined org. phases were dried ($MgSO_4$), and evaporated. Purification by bulb-to-bulb distillation (100°/0.5 torr) gave **41** (*ca.* 300 mg, *ca.* 97%) as a colorless oil. The ratio of enantiomers was determined by CGC (columns (*a*); heating rate: 80°/1° per min; pressure: 1.3 bar; t_R ((*R*)-**41**) *ca.* 43.9 min, t_R ((*S*)-**41**) *ca.* 44.7 min). The results are shown in *Table 1*.

Ti-TADDOLate-Catalyzed Addition of $MeTi(OCHMe_2)_3$ to PhCHO. (S)-1-Phenylethanol (**42**) (*GP III*). According to [45], the calculated amount of polymer-bound TADDOL (0.3 mmol) was suspended in toluene (10 ml) and stirred for 30 min, then the solvent was removed under h.v. at r.t. Toluene (15 ml) was added, and the suspension was cooled to −75°. Now, a stock soln. of 0.7M $MeTi(OCHMe_2)_3$ (3.0 ml, 2.1 mmol) in toluene was added. After stirring for 30 min at −75° and 1 h at r.t., the yellow suspension was recooled to −75°. PhCHO (140 µl, 1.36 mmol) was added and the suspension gradually warmed to 0° (*ca.* 16 h). After stirring for 5 h at 0° (ice-bath), workup according to *GP II*, and FC (pentane/Et_2O 4:1), **42** (*ca.* 120 mg, *ca.* 97%) was isolated as a colorless oil. The ratio of enantiomers was determined by CGC (column (*a*); heating rate: 80°/1° per min; pressure: 1.3 bar; t_R ((*R*)-**42**) *ca.* 34.5 min, t_R ((*S*)-**42**) *ca.* 35.8 min). For the results, see *Table 1*.

(S)-Nonan-3-ol (**43**). According to *GP II*, in the presence of polymer-bound Ti-TADDOLate, prepared from **23a** (720 mg, 0.45 mmol) and $Ti(OCHMe_2)_4$ (135 µl), heptanal (315 µl, 2.25 mmol) was treated with $Ti(OCHMe_2)_4$ (800 µl, 2.7 mmol) and Et_2Zn soln. (2.0 ml, 4.0 mmol, 2M in toluene). Stirring for 20 h at −30°, workup, and FC (pentane/Et_2O 3:1) gave **43** (244 mg, 75%) as a yellowish oil. The ratio of enantiomers was determined by ^{19}F-NMR spectroscopy of the corresponding *Mosher* derivatives [43]: (*S*)/(*R*) 96:4 (^{19}F-NMR (282.2 MHz): −71.79, −71.87).

(S)-1-Cyclohexylpropan-1-ol (**44**). According to *GP II*, in the presence of polymer-bound Ti-TADDOLate, prepared from **23a** (720 mg, 0.45 mmol) and $Ti(OCHMe_2)_4$ (135 µl), cyclohexanecarbaldehyde (210 µl, 2.25 mmol) was treated with $Ti(OCHMe_2)_4$ (800 µl, 2.7 mmol) and Et_2Zn soln. (2.0 ml, 4.0 mmol. 2M in toluene). Stirring for 20 h at −30°, workup, and FC (pentane/Et_2O 3:1) gave **44** (182 mg, 57%) as a colorless oil. The ratio of enantiomers was determined by CGC of the TFA derivatives [41] (column (*a*); heating rate: 80°/20 min then 0.6° per min; pressure: 1.5 bar; t_R ((*S*)-**44**) *ca.* 70.2 min, t_R ((*R*)-**44**) *ca.* 71.3 min): (*S*)/(*R*) 93:7.

(S)-1-Phenylpent-4-en-1-ol (**45**). According to [43], in the presence of polymer-bound Ti-TADDOLate, prepared from **23a** (720 mg, 0.45 mmol) and $Ti(OCHMe_2)_4$ (135 µl, see *GP II*), PhCHO (230 µl, 2.25 mmol) was treated with $(CH_2{=}CHCH_2CH_2)Ti(OCHMe_2)_3$ [43] (2.7 mmol) at −75°. The mixture was gradually warmed to 0° (*ca.* 16 h). After workup and purification by bulb-to-bulb distillation (145°/0.1 torr), **45** (145 mg, 40%) was isolated as a colorless oil. The ratio of enantiomers was determined by ^{19}F-NMR spectroscopy of the corresponding *Mosher* derivatives [43]: (*S*)/(*R*) 96:4 (^{19}F-NMR (282.2 MHz): −71.76, −72.06).

Opening of Cyclic meso-*Anhydrides. 1-Isopropyl (1R,2S)-cis-1,2,3,6-Tetrahydrophthalate* (**46**) (*GP IV*). According to [25], a suspension of polymer-bound diisopropoxy-Ti-TADDOLate, prepared according to *GP II* from **23a** (1.60 g, 1.01 mmol) and $Ti(OCHMe_2)_4$ (185 µl, 0.97 mmol) in toluene (10 ml), in THF (18 ml) was treated with *cis*-1,2,3,6-tetrahydrophthalic anhydride (122 mg, 0.8 mmol). After stirring for 9 d at −18° and workup according to *GP II*, **46** (109 mg, 35% conversion by GC) was isolated as a colorless solid. The ratio of enantiomers and the conversion were determined by CGC of the corresponding methyl isopropyl ester [25] (column (*c*); heating rate: 80°/30 min then 0.3°/min; pressure: 1.0 bar; t_R ((1*S*,2*R*)-**46**) *ca.* 130.4 min, t_R ((1*R*,2*S*)-**46**) *ca.* 131.5 min): e.r. > 95:5.

(2S,3R)-3-(Isopropyloxycarbonyl)bicyclo[2.2.1]hept-5-ene-2-carboxylic Acid (**47**). According to *GP IV*, a suspension of polymer-bound diisopropoxy-Ti-TADDOLate, prepared according to *GP II* from **23a** (1.60 g, 1.01 mmol) and $Ti(OCHMe_2)_4$ (285 µl, 0.97 mmol) in toluene (10 ml), in THF (18 ml) was treated with *cis-endo* bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride (132 mg, 0.8 mmol) at −18°. After stirring for 9 d at −18° and workup, **47** (160 mg, 85% conversion by GC) was isolated as a colorless solid. The ratio of enantiomers and the conversion were determined by CGC of the corresponding methyl isopropyl ester [25] (column (*b*); heating rate: 140° isotherm; pressure: 1.2 bar; t_R ((2*R*,3*S*)-**47**) *ca.* 53.5 min, t_R ((2*S*,3*R*)-**47**) *ca.* 55.4 min): e.r. =98:2.

LAH-TADDOLate Reductions of Acetophenone. Compound **42** (*GP V*). According to [8], THF (20 ml) was added to purified $LiAlH_4$ (40 mg, 1.05 mmol) and stirred for 15 min at r.t. The slightly muddy soln. was treated with EtOH (60 µl, 1.05 mmol), and, after stirring for a period of 15 min, the calculated amount of polymer-bound TADDOL (1.0 mmol) was added. The suspension was stirred for 45 min at r.t. At this time, the solvent was removed by syringe and the polymer washed twice with THF (*ca.* 15 ml). The mixture was cooled to −75°, acetophenone (58 µl, 0.5 mmol) was then added and allowed to warm to r.t. overnight (*ca.* 16 h). After hydrolysis with 1M aq. HCl soln. (20 ml), the mixture was filtered (glass filter *G2*). The polymer was washed with H_2O (50 ml), THF (10 ml), and Et_2O (50 ml). The phases were separated, the aq. layer extracted with Et_2O (2 × 50 ml), and the combined org. phases were washed with sat. aq. NaCl soln., dried ($MgSO_4$), and evaporated to give crude **42**. The ratio of the enantiomers and the conversion were determined by CGC (column (*a*); heating rate: 80°/1° per min; pressure: 1.3 bar; t_R (acetophenone ca. 24.1 min, t_R ((*R*)-**42**) *ca.* 34.4 min, t_R ((*S*)-**42**) *ca.* 35.8 min). For the results, see *Table 2*.

Ti-TADDOLate-Catalyzed Diels-Alder *Addition of 3-[(*E*)-Prop-2-enoyl]-1,3-oxazolidin-2-one to Cyclopentadiene. 3-[(3-Methylbicyclo[2.2.1]hept-5-en-2-yl)carbonyl]1,3-oxazolidin-2-one* (**48**) (*GP VI*). According to [2], the calculated amount of polymer-bound TADDOL (0.3 mmol) was suspended in toluene (10 ml) and stirred for 30 min, then the solvent was removed under h.v. at r.t. The polymer was suspended in toluene (15 ml), and a stock soln. of 0.224M $Cl_2Ti(OCHMe_2)_2$ (0.89 ml, 0.2 mmol) in toluene was added and stirred for *ca.* 16 h at r.t. The solvent was removed with a syringe and the polymer washed with toluene (3 × 10 ml). Toluene was added (15 ml) and the suspension cooled to *ca.* −20°. Successively, crotonoyl-oxazolidinone [91] (310 mg, 2.0 mmol) and cyclopentadiene (3.2 ml, 40.0 mmol; freshly prepared from dicyclopentadiene *via* heating up to 180–200°, followed by distillation of the monomer at 40° and subsequent cooling in a i-PrOH/CO_2 bath) were added and the suspension stirred for *ca.* 16 h. For workup, 1M aq. HCl soln. was added, 30 min stirred and filtered (glass filter *G2*). The polymer was washed with H_2O (50 ml), THF (10 ml), and Et_2O (50 ml). The phases were separated, the aq. layer extracted with Et_2O (2 × 50 ml), and the combined org. phases were washed with sat. aq. NaCl soln., dried ($MgSO_4$), and evaporated and the crude product dried under h.v. The *endo*/*exo*-ratio and the conversion were determined by ^{1}H-NMR (Me signals: *endo*-**48** 1.12 ppm, *exo*-**48** 0.84 ppm, crotonoyl-oxazolidinone 1.93 ppm). The ratio of the enantiomers was determined by reduction of a sample of the crude *Diels-Alder* adduct **48** with $LiAlH_4$ to the alcohol and CGC of the corresponding TFA derivative [2] (column (*c*); heating rate: 55°/0.2° per min; pressure: 1.2 bar; t_R (*endo*-(2*S*)-**48**) *ca.* 42.0 min, t_R (*endo*-(2*R*)-**48**) *ca.* 44.9 min; t_R (*exo*-adducts **48**) *ca.* 48.0 and 50.1 min). Purification by FC (Et_2O/pentane 2:1) gave the *Diels-Alder* adduct **48** as an *endo*/*exo*-mixture, the spectral data are identical to those in [51]. The results are shown in *Table 3*.

Ti-TADDOLate-Catalyzed 1,3-Dipolare Cycloaddition. 3-[(5-Methyl-2,3-diphenyl-1,3-isoxazolidin-4′-yl)-carbonyl]-1,3-oxazolidin-2-one (**49**) (*GP VII*). According to *GP VI*, polymer-bound TADDOL (0.3 mmol) was treated with $Cl_2Ti(OCHMe_2)_2$ (0.2 mmol) in toluene. To the resulting polymer-bound Ti-TADDOLate in toluene (20 ml) was added crotonoyl-oxazolidinone [91] (310 mg, 2.0 mmol) and nitrone [92] (775 mg, 3.9 mmol). After stirring for 2 d at r.t., the mixture was filtered over SiO_2 (3 cm × 2 cm), washed with toluene (50 ml) and CH_2Cl_2 (200 ml). The solvent was evaporated and the residue dried under h.v. The *exo*/*endo*-ratio and the conversion were determined by ^{1}H-NMR (Me signals: *exo*-**49** 1.46 ppm, *endo*-**49** 1.56 ppm, crotonoyl-oxazolidinone 1.93 ppm). The ratio of the enantiomers of *exo*-**49** was determined by ^{1}H-NMR using [Eu(hfc)$_3$] (separation of the Me signal at 1.46 ppm, *ca.* 10 mg of crude product and *ca.* 1–5 mg [Eu(hfc)$_3$]). Purification by FC (Et_2O/pentane 1:1→2:1) gave **49** as an *exo*/*endo*-mixture (M.p. 134–135° (*exo*-**49**); the spectral data are identical to those in [57]). The results are shown in *Table 4*.

7. *Use of the Dendrimer-bound TADDOLs. Ti-TADDOLate-Catalyzed Addition of Et_2Zn to PhCHO. Compound* **41**. According to [44], to a soln. of the calculated amount of dendrimer-bound TADDOL (0.4 mmol 'monomeric' TADDOL) in toluene (12 ml) was added $Ti(OCHMe_2)_4$ (120 µl, 0.4 mmol) and the resulting suspension stirred for *ca.* 4 h at r.t. The Me_2CHOH, liberated by ligand exchange, was removed with the solvent under h.v. at r.t., and the residue thus obtained was dried under h.v. for 3–4 h. Toluene (20 ml) was added and the resulting suspension cooled to *ca.* −30°. Successively, PhCHO (205 µl, 2.0 mmol), $Ti(OCHMe_2)_4$ (700 µl, 2.4 mmol), and Et_2Zn soln. (1.8 ml, 3.6 mmol, 2M in toluene) were added, and the mixture was stirred for *ca.* 16 h at *ca.* −30°. Workup according to *GP II* gave a solid, which was dissolved in CH_2Cl_2, and the soln. was treated with SiO_2 (*ca.* 2 g). The solvent was evaporated and the SiO_2 put on a FC column. *Compound* **41** was first eluated with pentane/Et_2O 1:1, then the dendrimer with CH_2Cl_2/AcOEt 25:1 (recovery of the dendrimer-bound TADDOL *ca.* 90%). The ratio of enantiomers was determined by CGC (column (*a*); heating rate: 80°/1° per min; pressure: 1.3 bar; t_R ((*R*)-**41**) *ca.* 43.9 min, t_R ((*S*)-**41**) *ca.* 44.7 min). The results are shown in *Table 1*.

Ti-TADDOLate-Catalyzed 1,3-Dipolare Cycloaddition. Compound **49**. According to [57], to a soln. of the calculated amount of dendrimer-bound TADDOL (0.25 mmol 'monomeric' TADDOL) in toluene (20 ml) was added a 0.224M stock soln. of $Cl_2Ti(OCHMe_2)_4$ (0.98 ml, 0.2 mmol) in toluene and stirred for *ca.* 4 h at r.t. The resulting yellowish, slightly muddy soln. was treated with crotonoyl-oxazolidinone [91] (310 mg, 2.0 mmol) and nitrone [92] (435 mg, 2.2 mmol). After stirring for 24 h at r.t., the mixture was treated with CH_2Cl_2/MeOH (19:1, 20 ml) and SiO_2 (*ca.* 2 g). The solvent was evaporated and the SiO_2 put on a FC column. Compound **49** was first eluated with Et_2O/pentane 3:1, then the dendrimer with CH_2Cl_2/AcOEt 25:1 (recovery of the dendrimer-bound TADDOL *ca.* 90%). The *exo*/*endo*-ratio and the conversion of **49** were determined by ^{1}H-NMR spectroscopy (Me signals: *exo*-**49** 1.46 ppm, *endo*-**49** 1.56 ppm, crotonoyl-oxazolidinone 1.93 ppm). The ratio of the enantiomers of *exo*-**49** was determined by ^{1}H-NMR using [Eu(hfc)$_3$] (separation of the Me signal at 1.46 ppm, *ca.* 10 mg of crude product and *ca.* 1–5 mg [Eu(hfc)$_3$]). The results are shown in *Table 4*.

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