Investigations of the Asymmetric Intramolecular [2 + 2] Photocycloaddition and Its Application as a Simple Access to Novel C_2-Symmetric Chelating Bisphosphanes Bearing a Cyclobutane Backbone

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The asymmetric intramolecular [2 + 2] photocycloaddition of α,β-enoates was evaluated as a simple access to the novel C_2-symmetric bisphosphanes **22** and **27** possessing a cyclobutane backbone. A source of different chiral auxiliaries for investigations of the photochemical key step was provided by the transacetalization of dialkyl tartrates **3** with the corresponding 3,3-dialkoxybutan-2-ones **4**. An insight into the selection mechanism was gained by temperature dependent measurements on the irradiation of the dicinnamates **10a**−**d**, since the corresponding Eyring diagram discloses strictly linear functions as well as an isoselective relationship. Diol **8a** turned out to be a structurally optimized auxiliary in terms of chiral induction and product crystallization and was also successfully applied in the first asymmetric photodimerization of 2-indenecarboxylic acid esters. Indeed, in this case excellent diastereoselectivities were achieved, too, but head-to-tail dimers **16a** and **16b** were formed predominantly. Diesters **11a** and **16a** were converted by standard procedures into the desired enantiopure 1,4-diphosphane **22** and 1,5-diphosphane **27**. Furthermore, the hitherto unknown absolute configuration of δ-truxinic acid was elucidated from a single crystal X-ray structure analysis of **11a**.

Introduction

The conformational properties of ligands are well-known to influence the reactivity and selectivity of transition metal catalysts.[1] This is particularly evident in the enantiodifferentiating hydrogenation catalyzed by rhodium(I) complexes bearing chelating bisphosphanes. By comparison of DIOP[2] and its carbocyclic analogues,[3] the effect of the conformational properties of the ligand backbone on the seven-membered rhodium(I) chelate ring which may adopt two extremely different conformations with a respective enantiomorphous arrangement of the *P*-phenyl groups[3b,4] has been clearly demonstrated. However not many efforts have been made on tuning catalytic properties by variation of the substitution pattern of the carbocyclic framework. The promising selectivities achieved in asymmetric rhodium(I)-catalyzed hydrogenations utilizing C4DIOP (**1**)[3a] (Chart 1) and its recently synthesized analogue MOCBP (**2**)[5] as chelating ligands prompted us to elaborate a new access to enantiopure chelating bisphosphanes bearing a cyclobutane backbone.

Retrosynthetic Analysis. Although the synthesis of MOCBP (**2**) via an asymmetric thermal [2 + 2] cycloaddition[5,6] is straightforward and proceeds with high diastereoselectivity, this approach is structurally restricted to the employment of ketene derivatives for the cyclobutane formation. Such limitations should be overcome by the use of an asymmetric [2 + 2] photocycloaddition, as it renders possible two orthogonal retrosynthetic scissions which are presented in Scheme 1. For our preliminary synthetic studies, the intramolecular variant of route A seemed to be most promising. Previous investigations had already revealed erythritol derivatives to be suitable chiral auxiliaries for the intramolecular photodimerization of cinnamic acid esters.[7] However, neither 2,3-*O*-isopropylidenerythritol nor 2,3-di-*O*-methylerythritol met all requirements for a synthetic application. Indeed, with the 1,4-dicinnamate of the latter one the corresponding (+)-δ-truxinate formed with a diastereoselectivity of 85%, but all attempts to isolate this diastereomer failed.[7]

Chart 1

1 2

Synthesis of Chiral Auxiliaries for the Photodimerization. With regard to these results, we expected the tartaric acid derived dioxanes **8a** and **8b**[8] to be optimized auxiliaries for the asymmetric [2 + 2] photocycloaddition, since the essential requirements are present in their structure. The stabilization of the *gauche* conformation of the hydroxymethylene groups is quite similar to that in 2,3-di-*O*-methylerythritol. Moreover, due to its well-defined conformation, a six-membered ring should promote crystallization and therefore purification of the diastereomeric cycloaddition products. The re-

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Scheme 1

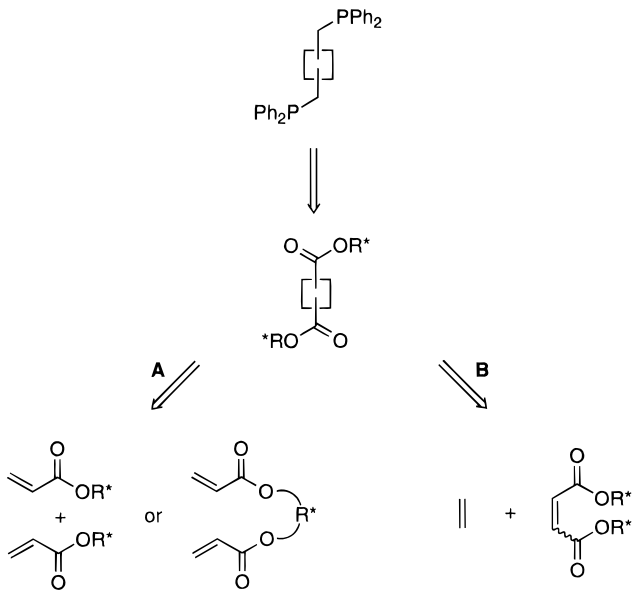

Table 1. Effect of Reaction Time on Transacetalization of Dialkyl Tartrates (3) with Corresponding 3,3-Dialkoxybutan-2-ones (4)

R	*t* (h)	**5**:**6**:**7**	yield (%)
a: Me[a]	4	81:12:7	–
	12	94:5:1	73 (**5a**)[b]
b: Et[d]	4	72:21:8	91 (md)[c]
	12	96:4:–	88 (md)[c]

[a] Reaction conditions: 60 °C, 40 mmHg. [b] Diastereomerically pure on crystallization. [c] Ratio of diastereomers remained unchanged after distillation. [d] Reaction conditions: 70 °C, 70 mmHg.

cently described transacetalization of diethyl tartrate **3b** with 3,3-dialkoxybutan-2-ones **4a** and **4b**[8,9] represents the key step in the synthesis of the diols **8a** and **8b**. In the course of our own investigations on the conversion with acetal **4b**, we established the necessity of prolonged reaction times for the attainment of high diastereomeric excesses. Quenching the reaction just after complete addition of **4b** afforded a mixture of all three possible diastereomeric 1,4-dioxanes, **5b**, **6b**, and **7b**, with only a moderate degree of stereoselectivity (Table 1 and Scheme 2). Separation of these three diastereomers was performed by subjecting this mixture to column chromatography. With a pure sample of 1,4-dioxane **6b** in hand we were able to refute the formerly made assumption that due to anomeric effects the formation of the diacetal **7b** with a 1,2-cis relationship should be more favored. Upon prolonged reaction time, **7b** even completely vanished and the reported 96:4 product distribution was attained.

For the synthesis of **8a** we intended to circumvent the disadvantages involved in the BF_3-mediated transacetalization of diethyl tartrate **3b** with **4a**, which, regardless of the reaction time, proceeded only with incomplete conversion and moderate selectivity.[8] A striking improvement was achieved by employing dimethyl tartrate **3a** instead of **3b** and slightly modifying the reaction conditions already applied for the synthesis of **5b**. Again, a reaction time of 12 h proved to be essential for the attainment of a good diastereoselectivity (Table 1). The main diastereomer **5a** could be easily obtained by crystallization from the crude reaction mixture. Column chromatography of the mother liquor furnished an inseparable 62:38 mixture of 1,4-dioxanes **5a** and **6a** as well as a pure sample of 1,4-dioxane **7a**. The coupling constant of 8.1 Hz between the two dioxane ring protons (determined from the ^{13}C-satellite) in **6a** indicates a remarkable deviation from the expected 1,2-trans−diaxial relationship. This phenomenon may be rationalized by a preference for a twist-boat conformation (Scheme 3) of the dioxane ring which has already been shown to be predominant in certain α-L-sorbopyranose derivatives.[10] Moreover, a twist-boat conformation possibly compensates for the destabilization caused by the anomeric effect in the chair conformation of **6a**. This assumption is consistent with the experimental results which rank the dioxanes **6a** and **6b** to be more stable than **7a** and **7b**.

With the diasteromerically pure ester **5a** as starting material, a clearly improved yield of the desired diol **8a** was achieved (Scheme 4). The minor diastereomer **9a** was obtained by reduction of a 62:38 mixture of diesters **5a** and **6a** and subsequent chromatographical separation. Reduction of a 96:4 mixture of diesters **5b** and **6b** yielded, upon crystallization of the crude product, diol **8b**. The minor compound **9b** was isolated from the mother liquor.

Stereoselective Intramolecular [2 + 2] Photocycloaddition of Dicinnamates and Di-2-indenoates. As the asymmetric photodimerization represents the crucial step in our new access to C4DIOP-related ligands, it was important to detect the relevant factors influencing its selectivity. For this purpose the dicinnamates **10a**−**d** were prepared from the corresponding diols by standard methodology. They were irradiated at different temperatures ranging from −75 to +45 °C in toluene as solvent to give the anticipated mixtures of the respective (+)-*δ*-**11a**−**d**, (−)-*δ*-**12a**−**d**, *β*-**13a**−**d** and neotruxinates **14a**−**c** (Scheme 5). The relative configuration of *δ*-truxinate **11a** was established by means of single crystal X-ray analysis.[11a] Upon conversion into the corresponding dimethyl ester with $SOCl_2$ in boiling methanol, it was shown to be a derivative of (+)-dimethyl *δ*-truxinate.[12] Thus, we were enabled to elucidate the correct absolute configuration of (+)-*δ*-truxinic acid, which turned out to be opposite of that previously assumed by Green.[7] The ratios of the diastereomeric cyclobutane products were determined by ^{13}C-NMR spectroscopy. In all cases the formation of **14a**−**c** was negligible and could only be established after chromatographical workup.

The Eyring plot (Figure 1) reveals two typical features of the asymmetric intramolecular [2 + 2] photocycloaddition. First, the ln *P* values (P = [**11**]/[**12**] = k(excess *δ*-truxinate)/k(minor *δ*-truxinate)) are found to be linearly dependent on the reciprocal of temperature in the whole temperature region investigated. On the basis of the principle of isoinversion,[13] this is equivalent to the existence of a single relevant partial step generating stereoselectivity in the cyclobutane formation. Furthermore, variation of the auxiliary discloses an isoselective relationship, as all four extrapolated curves intersect in

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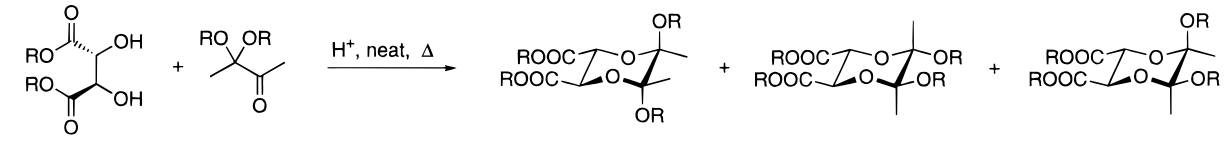
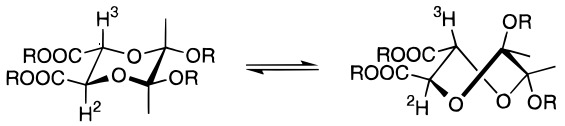
Scheme 2



R = Me **3a** **4a** **5a** **6a** **7a**
R = Et **3b** **4b** **5b** **6b** **7b**

Scheme 3

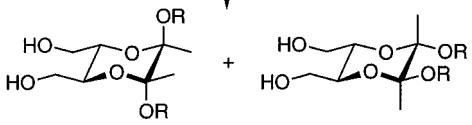


6 (chair) **6** (twist-boat)

Scheme 4[a]

a1:	**5a**	+	**6a**	100:0
a2:	**5a**	+	**6a**	62:38
b1:	**5b**	+	**6b**	96:4

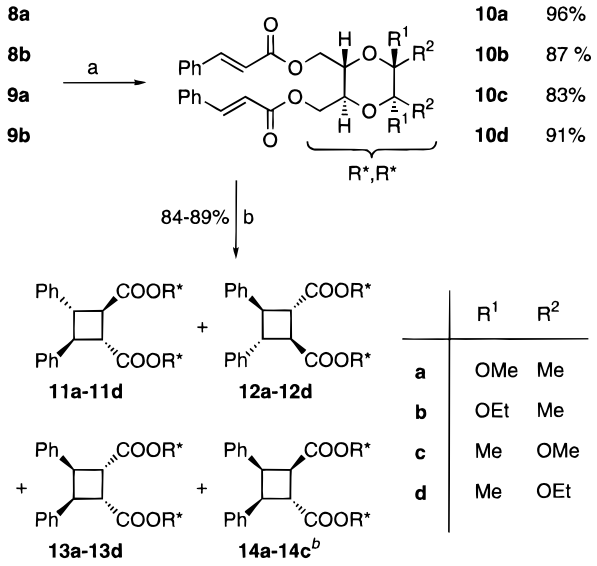
$LiAlH_4$, THF



a1:	**8a**	95%			R = Me
a2:	**8a**	57% (92%)[a]	**9a**	31% (91%)[a]	R = Me
b1:	**8b**	88% (92%)[a]	**9b**	3.6% (90%)[a]	R = Et

[a] Yields in parantheses refer to the corresponding diastereomer contained in the starting material.

Scheme 5[a]



[a] Key: (a) 2.2 equiv of PhCHCHCOCl, cat. DMAP, pyridine, CH_2Cl_2; (b) hν, *T*, 60 h, toluene. [b] Assignment of the absolute configuration of the cyclobutane moiety was arbitrary.

a narrow region close to 600 K. According to Giese,[14] this fact is interpreted as evidence for the diastereoselection to be introduced in all four cases on the basis of the same mechanism. From these facts we conclude the formation of the 1,4-diradical intermediate to be the dominant part in the selection step, whereas the competition between cyclization and fragmentation is only of minor importance

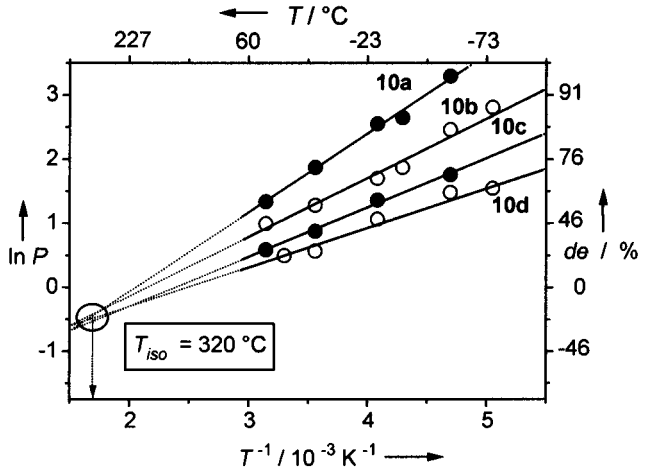


Figure 1. Eyring diagram for the competitive formation of diastereomeric δ-truxinates in the asymmetric intramolecular [2 + 2] photocycloaddition of dicinnamtes **10a**−**d** (see Scheme 5).

(Scheme 6). This result is in line with the observations made on the intermolecular photosensitized [2 + 2] photocycloaddition.[16] Concerning the competitive formation of δ-truxinates **11** and **12** versus β-truxinate **13**, a similiar temperature dependent relationship seems to exist (Table 2). Indeed, a diminishing selectivity for the latter one with decreasing temperature is observed, but the diastereomeric ratios determined by ^{13}C-NMR spectroscopy are not sufficiently exact for a quantitative evaluation. Some inaccuracy arises from the removal of C_2-symmetry in the β-truxinates **13** causing a double set of ^{13}C-NMR signals the NOE and spin relaxation effects of which differ from those of the δ-truxinates **11** and **12**.

The strong influence of the diacetal moiety on the diastereoselectivity discloses two essential properties of a structurally optimized auxiliary for the intramolecular [2 + 2] photocycloaddition. A stabilization of the 1,4-dioxane ring chair conformation due to a double anomeric effect caused by the 2,3-trans−diaxial relationship of the alkoxy substituents in **10a** and **10b** and a minimal number of degrees of freedom (comparison of methyl acetals **10a** and **10c** vs ethyl acetals **10b** and **10d**) are necessary to "fix" an advantageous *gauche* conformation of the (cinnamoyloxy)methylene groups. As a consequence of these requirements **10d** did not undergo any [2 + 2] cycloaddition upon irradiation at 45 °C.

Next, we expanded our investigations on the intramolecular [2 + 2] photocycloaddition of 2-indenecarboxy-

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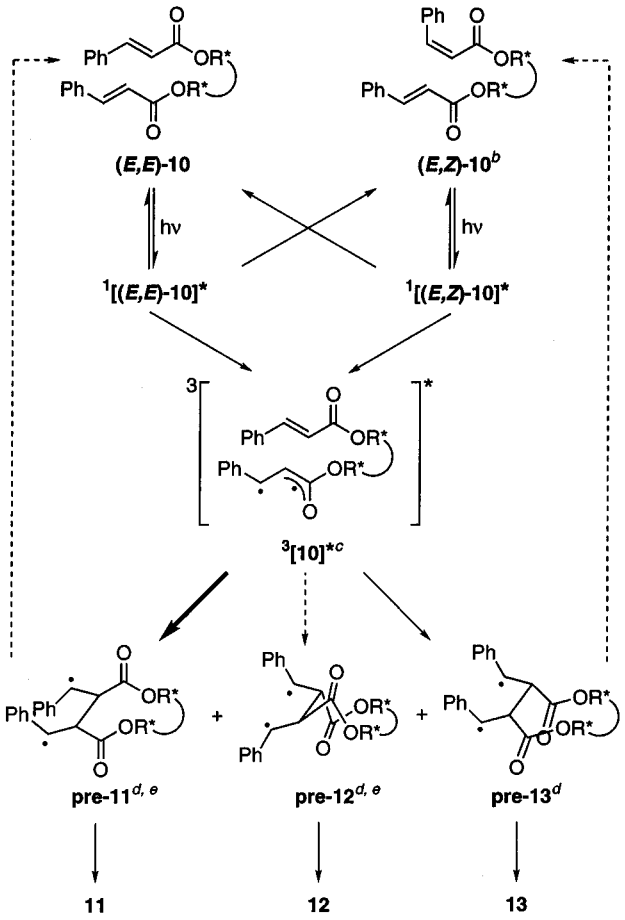
Scheme 6[a]



[a] The biradical mechanism illustrated in this scheme is adapted from that assumed for the [2 + 2] photocycloaddition of enones to olefines.[15] [b] *Z*/*E*-isomerization was established while controlling the conversion by NMR spectroscopy. [c] To simplify the illustration only one of the possible isomers and rotamers is shown. [d] The generation of the 1,4-biradicals proceeds presumably via exciplex formation.[15a] [e] **14** may be formed from rotamers of **pre-11** and **pre-12**.

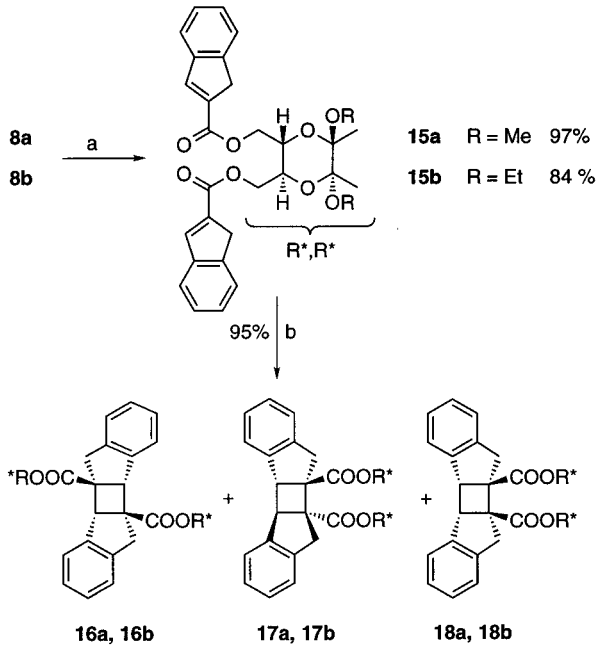
Table 2. Effect of Temperature and Auxiliary on Asymmetric Induction in the Intramolecular [2 + 2] Photocycloadditon of Dicinnamates (10a−d)

T (°C)	substrate	**11**:**12**:**13**
−60	**10a**	27.0:1:4.5
	10b	11.7:1:5.6
	10c	5.8:1:2.4
	10d	4.4:1:2.0
+8	**10a**	6.5:1:2.2
	10b	3.6:1:2.2
	10c	2.4:1:1.7
	10d	1.8:1:1.0

lates, which are already known to be suitable substrates for the achiral variant of this reaction.[17] The di-2-indenecarboxylates **15a** and **15b** were prepared following the esterification protocol of Neises and Steglich.[18]

Lacking any possibility of cis−trans isomerization, the cyclobutane formation required remarkably less reaction time than in the case of the corresponding dicinnamates **10a−d** and proceeded with almost quantitative yield. Even more dramatic is the difference in the regiochemical course of the reaction. Whereas irradiation of dicinnamates exclusively yielded head-to-head dimers, in the cycloaddition of their bridged analogues **15a** and **15b**, head-to-tail dimerization gained significantly in importance (Scheme 7 and Table 3). Regardless of the auxiliary and the temperature, *syn*-head-to-tail dimer **16**, the structure of which was determined from a single crystal X-ray analysis of **16a**,[11b] represents the main isomer. Besides, the formation of nearly equal amounts of two further isomers, *anti*-head-to-head dimer **17** and *syn*-head-to-head dimer **18**, was observed. Their structures were deduced from NMR spectroscopical measurements. The coupling constant of 9.1 Hz between the two cyclobutane ring protons in **18a** clearly indicates their vicinal relationship. Furthermore, due to anisotropic shielding of the aryl groups, the signals of the methylene protons adjacent to the aryl group in *syn*-additon products **16a** and **18a** are shifted to higher field (0.27−0.71 ppm) as compared with *anti*-addition product **17a**. On the contrary, in the latter the cyclobutane ring protons are shifted significantly to higher field (0.70−0.82 ppm).

Scheme 7[a]



[a] Key: (a) 2-indenecarboxylic acid, DCC, cat. DMAP, CH_2Cl_2; (b) hν, *T*, 36 h, toluene.

The excellent diastereoselectivities achieved in the *anti*-head-to-head addition as well as the *syn*-head-to-tail addition are in accordance with the good inductions observed for δ-truxinate formation. Therefore, we assume the formation of **11**, **16**, and **17** to be uniformly controlled by the same conformation of the diol moiety. The absolute configurational assignment of the cyclobutane ring of **17** has been made according to this assumption. Obviously, among the factors influencing the selectivity of cyclobutane formation, not only the auxiliary plays an important role but also the conformational properties of the enoate itself. Looking at suitable precursor conformations for the intramolecular cyclodimerization of **15** (illustrated in Scheme 8), one can see that the *s*-cis conformer leads to *anti*-head-to-head addition, whereas the *s*-trans conformer favors *syn*-head-to-tail addition.[19] Semiempirical calculations on the corresponding methyl esters as model compounds (Table 4) tend to support this interpretation, which requires a distinct preference of the *s*-cis conformation in the case of cinnamates. Moreover, in particular the *s*-cis precur-

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Scheme 8

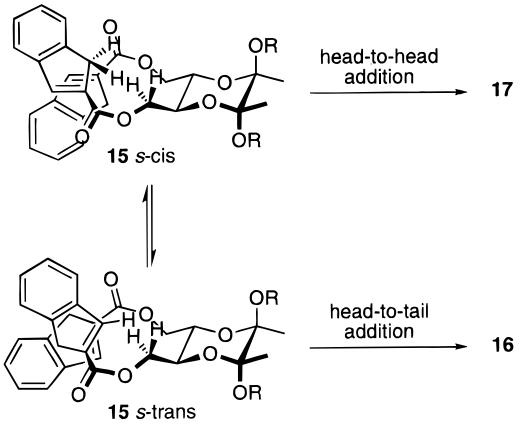


Table 3. Effect of Temperature and Auxiliary on Asymmetric Induction in the Intramolecular [2 + 2] Photocycloadditon of Di-2-indenoates (15a,b)

T (°C)	substrate	**16**:**17**:**18**
−70	**15a**	2.6:1:1.1
	15b	1.5:1:0.9
−40	**15a**	2.3:1:1.2
	15b	1.6:1:1.0

Table 4. Calculated Energy Differences between *s*-cis and *s*-trans Conformers of Methyl Cinnamate and Methyl 2-Indenoate

	ΔE^a (kJ mol^{-1})	
compound	AM1	MNDO
methyl cinnamate	−1.92	−3.43
methyl 2-indenoate	−0.03	+0.21

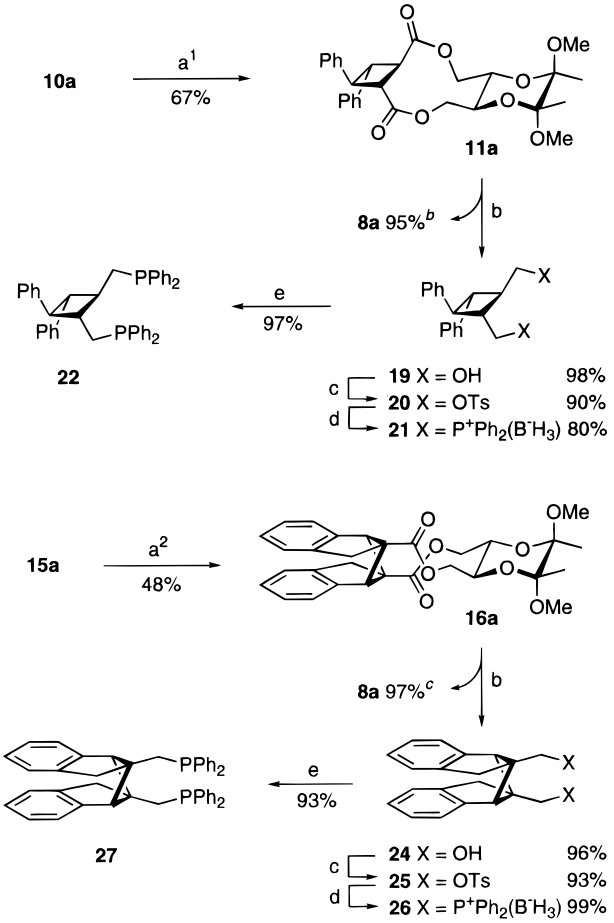
[a] $\Delta E = E(s\text{-cis}) - E(s\text{-trans})$.

sor conformation of **15** exhibits unfavorable nonbonded interactions between the protons of the two methylene groups. On the contrary, for the *s*-cis conformation of the corresponding dicinnamate **10**, such a destabilizating effect can be excluded.

Synthesis of Cyclobutane-Based C_2-Symmetric Ligands. Concerning the influence of the diacetal moiety of the auxiliary and the temperature, the above observations clearly exhibit the same tendencies for the intramolecular cylodimerization of dicinnamates **10a**−**d** (Table 2, Figure 1) as well as the di-2-indenoates **15a** and **15b** (Table 3). In every case, diol **8a** turns out to be the superior auxiliary, and the discrimination between the selectivities attainable with the auxiliaries **8a** and **8b** respectively increases with decreasing temperature. So, we focused our attention on the compounds **10a** and **15a** to elaborate a preparatively useful route to the desired enantiopure cyclobutanes **22** and **27** (Scheme 9). Irradiation of **10a** at low temperature and subsequent crystallization provided diastereomerically pure δ-truxinate **11a** in good yield. Preparation and purification of cyclobutane **16a** were performed in an analogous manner. Since this compound is hardly soluble in any common solvent and therefore its separation is easily feasible even on a multigram scale, we could tolerate the modest regioselectivity achieved in the irradiation of **15a**.

So far, the enantiopure diols **19** and **24** as well as the aspired diphosphanes **22** and **27** were prepared from **11a**

Scheme 9[a]



[a] Key: (a[1]) hν, −60 °C, 60 h, toluene; (a[2]) hν, −70 °C, 36 h, toluene; (b) $LiAlH_4$, THF; (c) TsCl, cat. DMAP, pyridine, CH_2Cl_2; (d) Li[$PPh_2(BH_3)$] (**23**), THF/DMF; (e) HBF_4OMe_2; Δ, CH_2Cl_2. [b] Overall recovery of **8a**: 61%. [c] Overall recovery of **8a**: 45%.

or **16a** in good to excellent yields employing established procedures. Particularly, the introduction of the diphenylphosphane group via the phosphane−borane adducts **21** and **26** proved to be a convenient method. It is noteworthy, that, in our hands, the protocol according to Le Corre[20] involving the *in-situ* generation of **23** from triphenylphosphane−borane adduct and lithium resulted in alternating, but in any case definitely lower, yields for the phosphanation step. Moreover, the use of DMF as cosolvent[21] turned out to be an essential factor for optimized reaction conditions. Finally, the complete protolytic decomplexation[21] of **21** and **26** to the free 1,4-diphosphane **22** and 1,5-diphosphane **27**, respectively, was accomplished at elevated temperature by constantly removing the liberated diborane.

Conclusions

We have elaborated a versatile asymmetric synthetic route to new C_2-symmetrical diphosphanes possessing a strongly substituted cyclobutane backbone. Representing the crucial step in this protocol, the asymmetric intramolecular [2 + 2] photocycloaddition was investigated in more detail to unveil the relevant factors determining its selectivity. On the basis of these results, diol **8a** is featured as a structurally optimized auxiliary, permitting

(19) The equilibrium between *s*-cis and *s*-trans conformers of α,β-enal complexes is also discussed to be a relevant factor determining the selectivity of catalytic Diels−Alder reactions: (a) Birney, D. M.; Houk, K. N. *J. Am. Chem. Soc.* **1990**, *112*, 4127. (b) Corey, E. J.; Loh, T.-P.; Roper, T. D.; Azimioara, M. D.; Noe, M. C. *J. Am. Chem. Soc.* **1992**, *114*, 8290.

(20) Brisset, H.; Gourdel, Y.; Pellon, P.; Le Corre, M. *Tetrahedron Lett.* **1993**, *34*, 4523.

(21) McKinstry, L.; Livinghouse, T. *Tetrahedron Lett.* **1994**, *35*, 9319.

us to perform the cyclodimerization of cinnamates and 2-indenoates with excellent diastereoselectivities on a preparative by useful multigram scale.

Current studies, in the group of Selke,[22] are aimed at uncovering the potential of diphosphanes **22** and **27** and their close relatives as ligands in transition- metal-catalyzed enantiodifferentiating syntheses. Results on the conversion of diesters **11a** and **16a** into the corresponding cyclobutane-based TADDOL analogues[23] and their application in asymmetric syntheses will be reported soon.

Experimental Section

General. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. THF was dried by the sodium−benzophenone method immediately prior to use. CH_2Cl_2 was distilled from $LiAlH_4$ in order to remove water and ethanol. Dry DMF was obtained by distillation from CaH_2. GC analyses were performed on a HP 5890 series II gas chromatograph equipped with a FFAP column (25 m × 0.32 mm), a flame ionization detector, and a HP 3396 A integrator. TLC was conducted with plates precoated with kieselgel 60 F_{254}. Unless otherwise noted, detection was first by UV (254 nm) and then charring with a solution of 1.0 g vanillin in 250:25:10 methanol−acetic acid−sulfuric acid. After extraction of aqueous solutions the combined organic layers were dried over $MgSO_4$. Evaporation of solvents was accomplished with a rotary evaporator. Melting points (Pyrex capillary) are uncorrected.

(2*R*,3*R*,5*R*,6*R*)-5,6-Dimethoxy-5,6-dimethyl[1,4]dioxane-2,3-dicarboxylic Acid Dimethyl Ester (5a). A 500 mL flask was fitted with a pressure-equalized dropping funnel and a 50 cm Vigreux column which was connected to a gas outlet leading to a condensing trap. The flask was charged with 134 g of L-(+)-dimethyl tartrate (**3a**) (0.75 mol) and 3 g of *p*-toluenesulfonic acid. After being heated to 70 °C, the trap was connected with a water aspirator and the pressure in the flask was adjusted to 70 mmHg. Then, 209 g of 3,3-dimethoxybutan-2-one (**4a**)[8] (1.58 mol) was added to the reaction mixture within 4 h. At this point of the reaction GC analysis revealed complete consumption of **3a** and a product distribution of **5a**, **6a**, and **7a** in a ratio of 81:12:7. After stirring for additional 8 h, 12 g of K_2CO_3 was added. As soon as the temperature had dropped below 60 °C the viscous reddish brown mixture was disolved in 250 mL of $CHCl_3$ and stirring was continued for another hour. This suspension was poured on 200 mL of water, the phases were separated, and the aqueous layer was extracted twice with 250 mL of $CHCl_3$. The combined organic phase was dried, filtered, and concentrated under reduced pressure. The product ratio of **5a**, **6a**, and **7a** was determined by GC analysis to be 94:5:1. The obtained brown mass was dissolved in a minimum of ether, and pentane was added until the solution became turbid. On standing in the refrigerator, the product crystallized to give 160 g of **5a** (73% based on **3a**) as colorless crystals. The filtrate was concentrated and distilled under high vacuum. The fraction boiling at 106−109 °C/0.01 mbar was collected to furnish 26.8 g of 1,4-dioxanes **5a**, **6a**, and **7a** as a 57:36:7 mixture of diastereomers. This material was subjected to column chromatography on 500 g of silica gel with 2:1 hexane−ethyl acetate to afford 22.1 g of a 62:38 mixture of diastereomers **5a** and **6a** (analytical data of **6a** refer to this mixture). Further elution with ether yielded 1.68 g of **7a** as a colorless oil. Detection was performed by charring with a solution of ammonium molybdate(VI) tetrahydrate in 10% aqueous H_2SO_4.

5a. Mp: 107 °C. $[\alpha]^{20}_D$: −110.4° (c = 1.13, $CHCl_3$). IR (KBr): 2993, 2841, 1738, 1364 cm^{-1}. MS (70 eV): m/z 261 (M − MeO)$^+$. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 1.36 (s, 6), 3.33 (s, 6), 3.77 (s, 6), 4.54 (s, 2, ^{13}C-satellite: dd, $^1J_{C,H}$ = 150.5 Hz, ^3J = 10.0 Hz). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 17.33, 48.46, 52.52, 68.76, 99.22, 168.44. Anal. Calcd for $C_{12}H_{20}O_8$: C, 49.31; H, 6.90. Found: C, 49.37; H, 6.97.

(2*R*,3*R*,5*S*,6*S*)-5,6-Dimethoxy-5,6-dimethyl[1,4]dioxane-2,3-dicarboxylic Acid Dimethyl Ester (6a). $[\alpha]^{20}_D$: −2.9° (c = 1.05, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 1.39 (s, 6), 3.39 (s, 6), 3.77 (s, 6), 4.83 (s, 2, ^{13}C-satellite: dd, $^1J_{C,H}$ = 152.2 Hz, ^3J = 8.1 Hz). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 18.16, 49.26, 52.40, 70.15, 100.36, 169.85. Anal. Calcd for $C_{12}H_{20}O_8$: C, 49.31; H, 6.90. Found: C, 49.38; H, 6.90.

(2*R*,3*R*,5*r*,6*s*)-5,6-Dimethoxy-5,6-dimethyl[1,4]dioxane-2,3-dicarboxylic Acid Dimethyl Ester (7a). $[\alpha]^{20}_D$: −14.5° (c = 0.94, $CHCl_3$). IR ($CHCl_3$): 3015, 2839, 1751, 757 cm^{-1}. MS (70 eV): m/z 261 (M − MeO)$^+$. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 1.32, 1.63 (2 s, 6), 3.36, 3.44 (2 s, 6), 3.76, 3.79 (2 s, 6), 4.50, 4.54 (2 d, 2, ^3J = 9.9 Hz). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 16.93, 17.57, 48.89, 50.06, 52.45, 52.59, 68.64, 72.50, 99.08, 100.03, 167.94, 168.69. Anal. Calcd for $C_{12}H_{20}O_8$: C, 49.31; H, 6.90. Found: C, 49.30; H, 6.97.

(2*R*,3*R*,5*R*,6*R*)-5,6-Diethoxy-5,6-dimethyl[1,4]dioxane-2,3-dicarboxylic Acid Diethyl Ester (5b). b1: This compound was prepared in analogy to the procedure for **5a** from 155 g of L-(+)-diethyl tartrate (**3b**) (0.75 mol), 3 g of *p*-toluenesulfonic acid, and 253 g of 3,3-diethoxybutan-2-one (**4b**)[8] (1.58 mol) at 60 °C/40 mmHg. After the workup procedure and distillation according to ref 8, 230 g of a 96:4 mixture of diastereomeric dioxanes **5b** and **6b** (88% based on **3b**) was obtained.

b2: A 71:21:8 mixture of diasteromeric 1,4-dioxanes **5b**, **6b**, and **7b** was produced by the same technique reported above from 5.00 g of **3b** (24.2 mmol), 0.10 g of *p*-toluenesulfonic acid, and 8.14 g of **4b** (50.8 mmol). The reaction was interrupted immediately after the addition of **4b** by addition of 0.5 g of K_2CO_3. The reaction mixture was stirred for another hour, filtered, and distilled to give 7.65 g of a mixture of 1,4-dioxanes (91% based on **3b**). 1.04 g of this slightly yellow oil was subjected to column chromatography on 400 g of silica gel with 7:1 hexane−ethyl acetate to afford in order of increasing polarity 201 mg of **6b**, 207 mg of a fraction containing a 95:5 mixture of **5b** and **6b**, 508 mg of **5b** and 77 mg of **7b**.

5b. $[\alpha]^{20}_D$: −111.5° (c = 1.14, $CHCl_3$). IR ($CHCl_3$): 2980, 2898, 1747, 1188 cm^{-1}. MS (70 eV): m/z 303 (M − EtO)$^+$. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 4.50 (^{13}C-satellite: dd, $^1J_{C,H}$ = 151.1 Hz, ^3J = 10.1 Hz). Remaining NMR data are in accordance with ref 8. Anal. Calcd for $C_{16}H_{28}O_8$: C, 55.16; H, 8.10. Found: C, 55.50; H, 8.40.

(2*R*,3*R*,5*S*,6*S*)-5,6-Diethoxy-5,6-dimethyl[1,4]dioxane-2,3-dicarboxylic Acid Diethyl Ester (6b). $[\alpha]^{20}_D$: +28.9° (c = 0.91, $CHCl_3$). IR ($CHCl_3$): 2981, 2898, 1752, 757 cm^{-1}. MS (70 eV): m/z 303 (M − EtO)$^+$. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 1.21 (t, 6, ^3J = 7.1 Hz), 1.28 (t, 6, ^3J = 7.1 Hz), 1.41 (s, 6), 3.57, 3.93 (2 dq, 4, $|^2J|$ = 8.9 Hz), 4.17, 4.23 (2 dq, 4, $|^2J|$ = 10.8 Hz), 4.82 (s, 2, ^{13}C-satellite: dd, $^1J_{C,H}$ = 156.6 Hz, ^3J = 10.4 Hz). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 14.03, 15.54, 19.18, 56.59, 61.44, 71.21, 100.37, 169.17. Anal. Calcd for $C_{16}H_{28}O_8$: C, 55.16; H, 8.10. Found: C, 55.54; H, 8.36.

(2*R*,3*R*,5*r*,6*s*)-5,6-Diethoxy-5,6-dimethyl[1,4]dioxane-2,3-dicarboxylic Acid Diethyl Ester (7b). $[\alpha]^{20}_D$: −24.6° (c = 1.58, $CHCl_3$). IR ($CHCl_3$): 2981, 2904, 1751, 1200 cm^{-1}. MS (70 eV): m/z 303 (M − EtO)$^+$. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 1.21, 1.28 (2 t, 6, ^3J = 7.1 Hz), 1.30 (t, 6, ^3J = 7.2 Hz), 1.33, 1.62 (2 s, 6), 3.61, 3.66 (2 dq, 2, $|^2J|$ = 9.7 Hz), 3.68, 3.88 (2 dq, 2, $|^2J|$ = 9.2 Hz), 4.21, 4.23 (2 q, 4), 4.50, 4.55 (2 d, 2, ^3J = 10.1 Hz). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 14.01 (2 C), 15.53, 15.63, 17.91, 18.97, 57.00, 58.28, 61.50 and 61.58, 68.76, 72.67, 99.27, 100.03, 167.67, 168.49. Anal. Calcd for $C_{16}H_{28}O_8$: C, 55.16; H, 8.10. Found: C, 55.33; H, 8.20.

(2*S*,3*S*,5*R*,6*R*)-2,3-Bis(hydroxymethyl)-5,6-dimethoxy-5,6-dimethyl[1,4]dioxane (8a). a1: To a stirred suspension of 24.1 g of $LiAlH_4$ (0.636 mol) in 400 mL of dry THF was added a solution of 155 g of diester **5a** (0.530 mol) in 250 mL of THF in portions at a rate maintaining gentle reflux. Afterwards, the reaction mixture was heated at reflux for 3 h. Hydrolysis of the excess $LiAlH_4$ was accomplished by careful additon of 10% KOH (~50 mL) just to the point that the gray slurry

(22) Rüdiger Selke, Max-Planck-Gesellschaft AG "Asymmetrische Katalyse" an der Universität Rostock, Germany.

(23) (a) Seebach, D.; Plattner, D. A.; Beck, A. K.; Wang, Y. M.; Hunziker, D.; Petter, W. *Helv. Chim. Acta* **1992**, *75*, 2171. (b) Ito, Y. N.; Ariza, X.; Beck, A. K.; Bohac, A.; Ganter, C.; Gawley, R. E.; Kuhnle, F. N. M.; Tuleja, J.; Wang, Y. M.; Seebach, D. *Helv. Chim. Acta* **1994**, *77*, 2071.

turned white. Then, the reaction mixture was heated at reflux for another hour. After filtration the white inorganic precipitate was extracted twice with 400 mL of boiling 95:5 THF−water. The combined THF solution was dried, filtered, and evaporated to give 126 g of a solid white residue. This residue was redissolved in a minimum of boiling ether. On standing in the refrigerator diol **8a** precipitated to give 119 g of colorless crystals (95% based on **5a**).

a2: A 62:38 mixture of diastereomeric diols **8a** and **9a** was prepared by the procedure described above from 20.0 g of a 62:38 mixture of diesters **5a** and **6a** (68.4 mmol) and 3.11 g of $LiAlH_4$ (82.0 mmol). After workup, 15.9 g of a white solid mass was obtained. Separation of the diastereomers was accomplished by column chromatography of three portions of 5.30 g on 400 g of silica gel with ethyl acetate. The less polar fraction furnished 5.58 g of **9a** (91% based on **6a**). Further elution yielded 9.20 g of the main diastereomer **8a** (92% based on **5a**).

8a. Mp: 120 °C. $[\alpha]^{20}_D$: −165.1° (c = 1.21, $CHCl_3$). IR (KBr): 3449, 3403, 2961, 2837, 1428, 857 cm^{-1}. MS (70 eV): m/z 205 $(M - MeO)^+$. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 2.95 ("t", 2, ^3J = 6 Hz, OH), 3.69 (m, 4), 3.79 (m, 2). Remaining NMR data in accordance with ref 8. Anal. Calcd for $C_{10}H_{20}O_6$: C, 50.84; H, 8.53. Found: C, 51.02; H, 8.48.

(2*S*,3*S*,5*S*,6*S*)-2,3-Bis(hydroxymethyl)-5,6-dimethoxy-5,6-dimethyl[1,4]dioxane (9a). Mp: 74 °C. $[\alpha]^{20}_D$: +100.4° (c = 1.01, $CHCl_3$). IR (KBr): 3471, 3306, 2951, 2836, 1309, 852 cm^{-1}. MS (70 eV): m/z 236 $(M)^+$. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 1.40 (s, 6), 2.94 (br s, 2), 3.34 (s, 6), 3.69 (m, 4), 4.03 (m, 2). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 17.60, 48.49, 63.13, 73.34, 100.51. Anal. Calcd for $C_{10}H_{20}O_6$: C, 50.84; H, 8.53. Found: C, 50.83; H, 8.50.

(2*R*,3*R*,5*S*,6*S*)-2,3-Diethoxy-5,6-bis(hydroxymethyl)-2,3-dimethyl[1,4]dioxane (8b). This compound was prepared in analogy to the procedure for **8a** from 174 g of diester **5b** (0.50 mol, de = 92%) and 22.8 g of $LiAlH_4$ (0.60 mol). The solid white residue (130 g) obtained after workup was recrystallized from ether−pentane to afford 116 g of **8b** (88% based on **5b**) as colorless needles. The mother liquor was concentrated in vacuum to give 9.8 g of a yellow oil containing a 59:41 mixture of diastereomers **9b** and **8b**. This residue was subjected to column chromatography on 500 g of silica gel with ethyl acetate to give 4.73 g of diol **9b** as a colorless solid followed by 3.16 g of diol **8b**. Mp: 121 °C. $[\alpha]^{20}_D$: −136.2° (c = 1.00, $CHCl_3$). IR (KBr): 3544, 3411, 2991, 2894, 1441, 854 cm^{-1}. MS (70 eV): m/z 219 $(M - EtO)^+$. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 3.51, 3.54 (2 dq, 4, $|^2J|$ = 9.4 Hz), 3.64, 3.70 (2 "dd", 4, $|^2J|$ = 12.1 Hz, ^3J = 4.5, 3.5 Hz). Remaining NMR data in accordance with ref 8. Anal. Calcd for $C_{12}H_{24}O_6$: C, 54.53; H, 9.15. Found: C, 54.75; H, 9.36.

(2*S*,3*S*,5*S*,6*S*)-2,3-Diethoxy-5,6-bis(hydroxymethyl)-2,3-dimethyl[1,4]dioxane (9b). Mp: 64 °C. $[\alpha]^{20}_D$: +68.1° (c = 1.00, $CHCl_3$). IR (KBr): 3394, 2977, 2877, 757 cm^{-1}. MS (70 eV): m/z 174 $(M - 2\ EtO)^+$. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 1.19 (t, 6, ^3J = 7.1 Hz), 1.41 (s, 6), 2.71 (br s, 2), 3.56, 3.72 (2 dq, 4, $|^2J|$ = 9.1 Hz), 3.67 (m, 4), 4.12 (m, 2). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 15.79, 18.67, 56.36, 63.31, 73.07, 100.41. Anal. Calcd for $C_{12}H_{24}O_6$: C, 54.53; H, 9.15. Found: C, 54.58; H, 9.14.

(2*S*,3*S*,5*R*,6*R*)-2,3-Bis(((*E*)-cinnamoyloxy)methyl)-5,6-dimethoxy-5,6-dimethyl[1,4]dioxane (10a). To a solution of 77.7 g of cinnamoyl chloride (0.466 mol) and 1.0 g of DMAP (8.2 mmol) in 150 mL of CH_2Cl_2 was dropped 50.0 g of diol **8a** (0.212 mol) in 300 mL of 1:1 pyridine−CH_2Cl_2 at a rate maintaining the temperature below 30 °C. After stirring the reaction mixture for 20 h at room temperature, 500 mL of CH_2Cl_2 and 600 mL of 2 M H_2SO_4 were added. The phases were separated, and the aqueous layer was extracted twice with 250 mL of CH_2Cl_2. The combined organic phase was washed with 200 mL of saturated $NaHCO_3$, dried, filtered, and concentrated under vacuum to give 118 g of a yellow oil. Crystallization from ethanol afforded 101 g of dicinnamate **10a** (96% based on **8a**) as colorless crystals. Mp: 138 °C. $[\alpha]^{20}_D$: −127.4° (c = 1.07, $CHCl_3$). IR (KBr): 3025, 2945, 2825, 1718, 1639 cm^{-1}. MS (70 eV): m/z 465 $(M - MeO)^+$. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 1.34 (s, 6), 3.31 (s, 6), 4.06 (m, 2), 4.30, 4.41 (2 "dd", 4, $|^2J|$ = 12.1 Hz, ^3J = 4.0, 4.7 Hz), 6.44 (d, 2, ^3J = 16.1 Hz), 7.29−7.48 (m, 10), 7.63 (d, 2). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 17.52, 48.04, 63.79, 67.80, 99.06, 117.52, 128.15, 128.83, 130.35, 134.23, 145.37, 166.58. Anal. Calcd for $C_{28}H_{32}O_8$: C, 67.73; H, 6.50. Found: C, 67.69; H, 6.64.

(2*S*,3*S*,5*R*,6*R*)-2,3-Bis(((indene-2-carbonyl)oxy)methyl)-5,6-dimethoxy-5,6-dimethyl[1,4]dioxane (15a). To a solution of 22.9 g of 2-indenecarboxylic acid[24] (143 mmol), 1.0 g of DMAP (8.2 mmol), and 15.6 g of diol **8a** (66.0 mmol) in 100 mL of CH_2Cl_2 was added 31.7 g of DCC (154 mmol) in 50 mL of CH_2Cl_2 at a rate maintaining the temperature below 30 °C. After stirring for 18 h the reaction mixture is filtered through Celite and evaporated under reduced pressure to give 42.1 g of a dark green oil. Crystallization from ethanol furnished 33.5 g of di-2-indenecarboxylate **15a** (97% based on **8a**) as slightly green crystals. Mp: 129 °C. $[\alpha]^{20}_D$: −133.9° (c = 0.90, $CHCl_3$). IR (KBr): 3019, 2948, 2823, 1703, 1567 cm^{-1}. MS (70 eV): m/z 489 $(M - MeO)^+$. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 1.34 (s, 6), 3.33 (s, 6), 3.50, 3.58 (2 dd, 4, $|^2J|$ = 13.8 Hz, ^4J = 2.0 Hz), 4.10 (m, 2), 4.38, 4.43 (2 "dd", 4, $|^2J|$ = 12.1 Hz, ^3J = 4.0, 4.7 Hz), 7.27−7.48 (m, 8), 7.62 (t, 2). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 17.49, 38.13, 48.02, 63.77, 67.96, 98.97, 123.49, 124.24, 126.86, 127.69, 136.52, 141.72, 142.50, 144.76, 164.40. Anal. Calcd for $C_{30}H_{32}O_8$: C, 69.22; H, 6.20. Found: C, 69.11; H, 6.20.

General Procedure for Irradiation of 10a−d, 15a, and 15b. All temperature-dependent measurements were carried out under nitrogen in a photoreactor which was fitted with an immersion well (vacuum jacket, Pyrex glass) and a high pressure mercury lamp HPK 125 W (Philips). The photoreactor was plunged in a thermostated bath and charged with a solution of 2.00 g of the respective compounds **10** and **15** in 200 mL of toluene. After 30 min of thermostatization, the solution was irradiated for 60 h in the case of **10** and 36 h in the case of **15**, respectively. Then, the solvent was evaporated and the ratio of the isomeric products was determined by ^{13}C-NMR spectra of the obtained slightly yellow solid residues. Separation and purification of the diasteromeric and regioisomeric products were accomplished by column chromatography and crystallization. Assignments were verified by NOE and COSY experiments, as well as by conversion of the diastereomeric truxinates into the corresponding dimethyl truxinates by treatment with $SOCl_2$ in boiling methanol.[7,12]

Irradiation of 10a. The residue obtained upon irradiation of 2.00 g of **10a** at −28 °C was chromatographed on 220 g of silica gel with 4:1 hexane−ethyl acetate to give in order of increasing polarity **12a** (colorless needles upon recrystallization from ethyl acetate−hexane), **13a** (foamy colorless solid), **11a** (colorless hexagonal prisms upon recrystallization from ether), and **14a** (colorless wax) along with fractions containing mixtures of diastereomers. The total amount of truxinates was 1.78 g (89% based on **10a**).

(−)-*δ*-Truxinate 12a. Mp: 220 °C. $[\alpha]^{20}_D$: −74.1° (c = 1.02, $CHCl_3$). IR (KBr): 3028, 2954, 2829, 1738, 1605, 1429, 886 cm^{-1}. MS (70 eV): m/z 465 $(M - MeO)^+$. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 1.29 (s, 6), 3.08 (half of AA′BB′ pattern, 2), 3.26 (s, 6), 3.88 (half of AA′BB′ pattern, 2), 3.90 (m, 2), 3.97 (dd, 2, $|^2J|$ = 11.1 Hz, ^3J = 2.0 Hz), 4.37 ("dd", 2, ^3J = 10.1 Hz), 7.19−7.33 (m, 10). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 17.27, 44.42, 48.20, 49.92, 66.11, 69.91, 98.85, 126.78, 127.25, 128.67, 139.84, 170.94. Anal. Calcd for $C_{28}H_{32}O_8$: C, 67.73; H, 6.50. Found: C, 68.06; H, 6.51.

***β*-Truxinate 13a.** Mp: 76 °C. $[\alpha]^{20}_D$: −74.2° (c = 0.95, $CHCl_3$). IR (KBr): 3029, 2957, 2834, 1741, 1605, 1249 cm^{-1}. MS (70 eV): m/z 465 $(M - MeO)^+$. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 1.30 (s, 6), 3.30 (s, 6), 3.80 (dd, 1, ^3J = 10.2, 5.5 Hz), 3.94 (dd, 1, ^3J = 6.4 Hz), 3.99, 4.03 (2 m, 2), 4.14 (dd, 1, $|^2J|$ = 11.8 Hz, ^3J = 3.4 Hz), 4.27 (dd, 1, $|^2J|$ = 11.8 Hz, ^3J = 4.0 Hz), 4.45 (m, 2, PhCH), 4.55 (dd, 1, ^3J = 7.9 Hz), 4.71 (dd, 1, ^3J = 9.1 Hz), 6.90 (m, 2), 6.93 (m, 2), 7.01−7.14 (m, 6). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 17.36 (2 C), 44.24, 44.60, 44.69, 44.73, 48.38 (2 C), 64.43, 64.70, 67.98, 68.55, 98.38 (2 C), 126.51, 126.55, 127.61, 127.79, 128.08, 128.12, 137.89, 137.95, 170.86, 171.28. Anal. Calcd for $C_{28}H_{32}O_8$: C, 67.73; H, 6.50. Found: C, 68.09; H, 6.71.

(24) Treibs, W.; Orttmann, H. *Chem. Ber.* **1960**, *93*, 545.

(+)-δ-Truxinate 11a. Mp: 174 °C. $[\alpha]^{20}_D$: +12.2° (*c* = 1.00, $CHCl_3$). IR (KBr): 3027, 2961, 2835, 1747, 1603, 1422, 1077 cm^{-1}. MS (70 eV): *m/z* 465 $(M - MeO)^+$. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 1.31 (s, 6), 3.17 (half of AA′BB′ pattern, 2), 3.28 (s, 6), 3.86 (half of AA′BB′ pattern, 2), 3.99 (m, 2), 4.03 (m, 2), 4.61 (dd, 2, $|^2J| = 12.1$ Hz, $^3J = 2.4$ Hz), 7.19−7.34 (m, 10). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 17.36, 44.52, 48.13, 50.20, 65.28, 67.62, 99.45, 126.76, 127.27, 128.67, 139.73, 171.53. Anal. Calcd for $C_{28}H_{32}O_8$: C, 67.73; H, 6.50. Found: C, 67.48; H, 6.57.

Neotruxinate 14a. $[\alpha]^{20}_D$: −13.7° (*c* = 1.41, $CHCl_3$). IR ($CHCl_3$): 3029, 2953, 2834, 1750, 1605, 1413 cm^{-1}. MS (70 eV): *m/z* 465 $(M - MeO)^+$. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 1.29, 1.33 (2 s, 6), 3.24, 3.29 (2 s, 6), 3.56 (dd, 1, $^3J = 11.8$, 8.1 Hz), 3.83 ("dd", 1, $|^2J| = 11.6$ Hz, $^3J = 5.9$ Hz), 4.03−4.11 (m, 3), 4.12 (t, 1, $^3J = 11.8$ Hz), 4.13 (t, 1, $^3J = 8.2$ Hz), 4.33 (dd, 1), 4.53 (dd, 1, $|^2J| = 11.8$ Hz, $^3J = 3.0$ Hz), 4.65 (m, 1), 6.87 (m, 2), 7.02−7.19 (m, 8). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 17.41 (2 C), 42.16, 45.53, 45.74, 48.14, 48.24, 49.22, 64.22, 65.36, 67.37, 68.04, 99.44, 99.60, 126.31, 126.74, 127.65, 128.12, 130.13, 134.81, 137.41, 169.33, 172.55. Anal. Calcd for $C_{28}H_{32}O_8$: C, 67.73; H, 6.50. Found: C, 67.97; H, 6.67.

Irradiation of 15a. The residue obtained upon irradiation of 2.00 g of **15a** at −40 °C was suspended in 10 mL of CH_2Cl_2 and filtered off to yield pure **16a** as a white powder (suitable crystals for X-ray analysis upon recrystallization from CH_2Cl_2). The filtrate was concentrated and chromatographed on 220 g of silica gel with 4:1 hexane−ethyl acetate to give in order of increasing polarity **18a** (colorless needles upon recrystallization from ether), **17a** (foamy colorless solid), and **16a** along with fractions containing mixtures of isomers. The total amount of indene-2-carboxylate dimers was 1.92 g (96% based on **15a**).

***syn*-Head-to-Head Indene-2-carboxylate Dimer 18a.** Mp: 233 °C. $[\alpha]^{20}_D$: −37.0° (*c* = 1.06, $CHCl_3$). IR (KBr): 3012, 2956, 2832, 1745, 1207 cm^{-1}. MS (70 eV): *m/z* 489 $(M - MeO)^+$. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 1.30 (s, 6), 3.23 (d, 1, $|^2J| = 18.0$ Hz), 3.28 (d, 1, $|^2J| = 17.5$ Hz), 3.30, 3.32 (2 s, 6), 3.33 (d, 1), 3.43 (d, 1), 4.00, 4.08 (2 td, 2, $^3J = 9.4$, 4.0 Hz), 4.12, 4.16 (2 dd, 2, $|^2J| = 11.4$ Hz, $^3J = 4.0$ Hz), 4.56, 4.60 (2 d, 2, $^3J = 9.1$ Hz), 4.65, 4.70 (2 dd, 2), 6.82−6.99 (m, 8). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 17.39 (2 C), 37.18, 37.64, 48.50, 48.56, 51.89, 51.96, 56.07, 56.59, 64.19, 64.37, 67.64, 67.70, 97.71 (2 C), 124.01, 124.08, 125.37, 125.72, 126.36, 126.41, 126.92, 140.23, 140.46, 142.86, 143.27, 173.83, 174.06. Anal. Calcd for $C_{30}H_{32}O_8$: C, 69.22; H, 6.20. Found: C, 69.13; H, 6.17.

***anti*-Head-to-Head Indene-2-carboxylate Dimer 17a.** Mp: 235 °C. $[\alpha]^{20}_D$: −40.2° (*c* = 1.03, $CHCl_3$). IR (KBr): 3022, 2956, 2833, 1747, 1736, 1198, 1013 cm^{-1}. MS (70 eV): *m/z* 489 $(M - MeO)^+$. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 1.34 (s, 6), 3.32 (s, 6), 3.70 (d, 2, $|^2J| = 18.0$ Hz), 3.78 (s, 2), 3.82 (d, 2), 4.04 (m, 2), 4.06 (m, 2), 4.64 (m, 2), 7.09−7.28 (m, 8). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 17.44, 38.05, 48.16, 53.25, 60.44, 65.25, 67.97, 99.24, 122.95, 124.62, 126.84, 127.30, 143.05, 143.16, 170.56. Anal. Calcd for $C_{30}H_{32}O_8$: C, 69.22; H, 6.20. Found: C, 69.04; H, 6.25.

***syn*-Head-to-Tail Indene-2-carboxylate Dimer 16a.** Mp: >270 °C. $[\alpha]^{20}_D$: −228.0° (*c* = 0.84, $CHCl_3$). IR (KBr): 3020, 2961, 2832, 1719, 1441, 1437, 1346 cm^{-1}. MS (70 eV): *m/z* 489 $(M - MeO)^+$. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 1.33 (s, 6), 3.11, 3.25 (2 d, 4, $|^2J| = 17.0$ Hz), 3.33 (s, 6), 4.12 (m, 2), 4.38 ("dd", 2, $|^2J| = 11.8$ Hz, $^3J = 7.1$ Hz), 4.48 (s, 2), 4.55 (dd, 2, $^3J = 2.8$ Hz), 6.73 (m, 2), 6.93 (m, 2), 7.06 (m, 2), 7.11 (m, 2). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 17.40, 37.20, 48.28, 54.89, 55.32, 65.58, 68.86, 98.97, 124.15, 125.37, 126.12, 127.45, 138.44, 143.35, 175.70. Anal. Calcd for $C_{30}H_{32}O_8$: C, 69.22; H, 6.20. Found: C, 69.33; H, 6.33.

(1*R*,5*S*,7*R*,8*R*,10*S*,14*R*,15*S*,16*S*)-7,8-Dimethoxy-7,8-dimethyl-2,13-dioxo-15,16-diphenyl-3,6,9,12-tetraoxatricyclo-[12.2.0.0^{5,10}]hexadecane (11a). Eight portions of 3.00 g of dicinnamate **10a** (48.3 mmol) were irradiated respectively in 200 mL of toluene for 60 h at −60 °C. Then, the combined toluene solutions were concentrated in vacuum to give 25.6 g of a solid yellow residue, which was roughly purified by column chromatography on 450 g of silica gel with 4:1 hexane−ethyl acetate. The obtained slightly yellow solid (18.5 g) was redissolved in ether, and pentane was added until the solution became turbid. On standing in the refrigerator, the product crystallized to give 16.1 g of **11a** (67% based on **10a**) as colorless, hexagonal prisms.

(1*S*,5*S*,7*R*,8*R*,10*S*,14*S*,15*S*,19*S*)-Dibenzo-7,8-dimethoxy-7,8-dimethyl-2,13-dioxo-3,6,9,12-tetraoxapentacyclo-[12.4.4.0^{5,10}.0^{1,15}.0^{14,19}]docosa-16,20-diene (16a). Ten portions of 3.34 g of di-2-indenecarboxylate **15a** (64.2 mmol) were irradiated respectively in 220 mL of toluene for 36 h at −70 °C. On concentrating the combined toluene solutions to 300 mL, product **16a** precipitated. The crystals were filtered off and washed with ether to give 15.4 g of **16a** as a colorless powder. A second crop of 0.6 g of **16a** was obtained from the mother liquor upon crystallization from CH_2Cl_2−pentane (total yield of 16.0 g, 48% based on **15a**).

(1*R*,2*R*,3*S*,4*S*)-1,2-Bis(hydroxymethyl)-3,4-diphenylcyclobutane (19). To a stirred suspension of 1.13 g of $LiAlH_4$ (29.8 mmol) in 100 mL of dry THF was added 9.85 g of diester **11a** (19.8 mmol) in portions at a rate maintaining gentle reflux. The reaction mixture was allowed to cool to ambient temperature and stirred for 3 h. Hydrolysis of the excess $LiAlH_4$ was accomplished by careful addition of 10% KOH (∼5 mL) just to the point that the gray slurry turned white. Then, the reaction mixture was heated at reflux for another hour. After filtration the white precipitate was extracted twice with 50 mL of boiling 95:5 THF−water. The combined THF solution was dried, filtered, and evaporated to give 10.34 g of a solid white residue. This residue was suspended in 150 mL boiling ether, concentrated to 60 mL, and filtered off to give 4.47 g of diol **19**. A second crop of 0.75 g of **19** (total yield of 5.32 g, 98% based on **11a**) was obtained from the mother liquor by complete removal of ether and subsequent crystallization from 8 mL of ethanol. The filtrate was concentrated under reduced pressure, and the residue was redissolved in a minimum of ether. On standing in the refrigerator, diol **8a** precipitated to give 4.50 g of colorless crystals (95% based on **11a**). Mp: 122 °C. $[\alpha]^{20}_D$: −83.4° (*c* = 1.06, $CHCl_3$). IR (KBr): 3343, 3279, 3026, 2926, 2864, 1602 cm^{-1}. MS (70 eV): *m/z* 268 $(M)^+$, 134 $(M/2)^+$. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 2.37 (m, 2), 3.12 (br s, 2), 3.16 (half of AA′BB′ pattern, 2), 3.60 ("t", 2, $|^2J| \sim {}^3J = 9.7$ Hz), 3.92 (dd, 2, $|^2J| = 10.2$ Hz, $^3J = 3.5$ Hz), 7.17−7.33 (m, 10). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 47.29, 47.52, 65.32, 126.60, 126.80, 128.54, 142.35. Anal. Calcd for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.29; H, 7.51.

(1*S*,2*S*,6*S*,7*S*)-Dibenzo-1,6-bis(hydroxymethyl)tricyclo-[5.3.0.0^{2,6}]deca-3,8-diene (24). This compound was prepared in analogy to the procedure for **19** from 1.18 g of $LiAlH_4$ (31.1 mmol) and 10.8 g of diester **16a** (20.7 mmol) in 125 mL of THF. The crude product (11.4 g) was purified by column chromatography on 220 g silica gel with 6:1 ethyl acetate−hexane to furnish 5.81 g of diol **24** (96% based on **16a**) as a white solid. Further elution with pure ethyl acetate gave 4.73 g of diol **8a** (97% based on **16a**). Mp: 138 °C. $[\alpha]^{20}_D$: −247.5° (*c* = 1.12, $CHCl_3$). IR (KBr): 3221, 3018, 2922, 2832 cm^{-1}. MS (70 eV): *m/z* 292 $(M)^+$, 146 $(M/2)^+$. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 2.53, 2.66 (2 d, 4, $|^2J| = 17.3$ Hz), 3.88 (s, 4), 3.92 (br s, 2), 3.94 (s, 2), 6.82 (m, 2), 6.97 (m, 2), 7.06 (m, 2), 7.09 (m, 2). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 37.92, 50.07, 50.68, 69.06, 124.55, 125.98, 126.03, 126.62, 142.43, 144.79. Anal. Calcd for $C_{20}H_{20}O_2$: C, 82.16; H, 6.90. Found: C, 82.03; H, 7.12.

(1*S*,2*S*,3*R*,4*R*)-1,2-Diphenyl-3,4-bis(((tolyl-4-sulfonyl)-oxy)methyl)cyclobutane (20). To a solution of 11.8 g of tosyl chloride (62.0 mmol) and 0.49 g of DMAP (4.0 mmol) in 60 mL of 25:10 CH_2Cl_2−pyridine was added 45 mL of a solution of 5.55 g of diol **19** (20.7 mmol) in 25:10 CH_2Cl_2−pyridine. The reaction mixture was stirred at ambient temperature for ∼12 h until TLC (1:1 hexane−ethyl acetate) indicated nearly complete conversion and new less polar compound appeared. To hydrolyze the excess tosyl chloride, 10 mL of water was added and the mixture was stirred for two more hours. After neutralization with 2 M H_2SO_4, the phases were separated, and the aqueous layer was extracted twice with 100 mL of CH_2Cl_2. The combined organic phase was washed with 50 mL of saturated $NaHCO_3$, dried, filtered, and concentrated under vacuum to give 12.9 g of a yellow oil. Crystallization from methanol afforded 10.73 g of ditosylate **20** (90% based on **19**) as colorless crystals. Mp: 121 °C. $[\alpha]^{20}_D$:

−32.3° (c = 1.04, $CHCl_3$). IR (KBr): 3028, 2924, 1598, 1369, 1174 cm^{-1}. MS (70 eV): m/z 288 $(M/2)^+$. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 2.44 (s, 6), 2.50 (m, 2), 3.25 (half of AA′BB′ pattern, 2), 4.09 ("dd", 2, $|^2J|$ = 10.6 Hz, ^3J = 4.0 Hz), 4.13 ("dd", 2, ^3J = 3.7 Hz), 7.06 (m, 4), 7.16−7.28 (m, 6), 7.33 (m, 4), 7.76 (m, 4). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 21.65, 40.77, 46.12, 70.19, 126.86, 126.90, 127.90, 128.58, 129.99, 132.88, 141.01, 145.00. Anal. Calcd for $C_{32}H_{32}O_6S_2$: C, 66.64; H, 5.59. Found: C, 66.42; H, 5.59.

(1*S*,2*S*,6*S*,7*S*)-Dibenzo-1,6-bis(((tolyl-4-sulfonyl)oxy)-methyl)tricyclo[5.3.0.0^{2,6}]deca-3,8-diene (25). This compound was prepared in analogy to the procedure for **20** from 11.3 g of tosyl chloride (59.4 mmol), 0.49 g of DMAP (4.0 mmol), and 5.78 g of diol **24** (19.8 mmol) in 105 mL of 25:10 CH_2Cl_2−pyridine. Purification of the crude product (12.7 g) was accomplished by column chromatography on 220 g of silica gel. After removal of less polar impurities with 6:1 hexane−ethyl acetate, elution with 3:2 hexane−ethyl acetate furnished 11.0 g of ditosylate **25** (93% based on **24**) as a colorless solid. Mp: 65 °C. $[\alpha]^{20}_D$: −92.2° (c = 0.95, $CHCl_3$). IR (KBr): 3022, 2923, 2844, 1598, 1361, 1177 cm^{-1}. MS (70 eV): m/z 428 $(M - TsOH)^+$, 300 $(M/2)^+$. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 2.45 (s, 6), 2.56, 2.66 (2 d, 4, $|^2J|$ = 17.3 Hz), 3.58 (s, 2), 4.16, 4.32 (2 d, 4, $|^2J|$ = 9.7 Hz), 6.76 (m, 2), 6.97 (m, 2), 6.99 (m, 2), 7.09 (m, 2), 7.38 (m, 2), 7.86 (m, 2). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 21.67, 37.73, 47.82, 51.86, 75.33, 124.49, 125.90, 126.36, 127.20, 128.00, 130.07, 132.75, 140.40, 143.88, 145.07. Anal. Calcd for $C_{34}H_{32}O_6S_2$: C, 67.98; H, 5.37. Found: C, 67.66; H, 5.18.

(1*R*,2*R*,3*S*,4*S*)-1,2-Bis((boranatodiphenylphosphanyl)-methyl)-3,4-diphenylcyclobutane (21). The reaction was conducted under an Ar atmosphere in a flame-dried Schlenk flask fitted with a rubber septum. To a solution of 1.00 g of diphenylphosphane−borane[25] (4.99 mmol) in 3.0 mL of THF at 0 °C was added 3.12 mL of 1.6 M *n*-butyllithium (4.99 mmol) in hexane. The resulting slightly turbid solution was stirred at 0 °C for 1 h, cooled to −50 °C, and treated with a solution prepared from 1.20 g of ditosylate **20** (2.08 mmol) and 4.0 mL of DMF in a seperate Schlenk flask under an Ar atmosphere. The mixture was allowed to warm to ambient temperature over 3 h and stirred for additional 16 h. Then, the reaction mixture was poured on 20 mL of saturated NH_4Cl, and the aqueous layer was extracted four times with 25 mL of toluene. The combined organic phase was dried, filtered, and evaporated in vacuum to give 1.4 g of a white solid. The crude product was recrystallized from ethanol to furnish 1.05 g of **21** (80% based on **20**) as colorless crystals. Mp: 156 °C. $[\alpha]^{20}_D$: +11.1° (c = 1.13, $CHCl_3$). IR (KBr): 3056, 3026, 2925, 2375, 2343, 1602, 1437 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 0.5−1.3 (br s, 6), 2.43 (ddd, 2, $|^2J|$ = 15.0 Hz, $|^2J|_{P,H}$ = 11.3 Hz, ^3J = 4.9 Hz), 2.50 (ddd, 2, $|^2J|_{P,H}$ = 13.0 Hz, ^3J = 6.6 Hz), 2.66 (half of AA′BB′ pattern, 2), 2.79 (m, 2), 6.76 (m, 4), 7.05−7.08 (m, 6), 7.21 (m, 4), 7.30−7.38 (m, 8), 7.44 (m, 4), 7.52 (m, 4). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 31.56 (d, $|^1J|_{P,C}$ = 34.2 Hz), 40.53 (d, $|^2J|_{P,C}$ = 9.2 Hz), 55.04 (d, $|^3J|_{P,C}$ = 6.1 Hz), 126.22, 127.04, 128.09, 128.60 (d, $|^3J|_{P,C}$ = 10.3 Hz), 128.88 (d, $|^3J|_{P,C}$ = 9.8 Hz), 129.40, 130.07 (d, $|^1J|_{P,C}$ = 55.5 Hz), 131.01 (d, $|^4J|_{P,C}$ = 2.5 Hz), 131.07 (d, $|^4J|_{P,C}$ = 2.4 Hz), 131.86 (d, $|^2J|_{P,C}$ = 9.2 Hz), 132.10 (d, $|^2J|_{P,C}$ = 9.1 Hz), 140.51. ^{31}P-NMR (203 MHz, $CDCl_3$): δ +12.22. ^{11}B-NMR (160 MHz, $CDCl_3$): δ −39.65. Anal. Calcd for $C_{42}H_{44}P_2B_2$: C, 79.77; H, 7.01. Found: C, 79.91; H, 7.21.

(1*S*,2*S*,6*S*,7*S*)-Dibenzo-1,6-bis((boranatodiphenylphosphanyl)methyl)tricyclo[5.3.0.0^{2,6}]deca-3,8-diene (26). This compound was prepared in analogy to the procedure for **21** from 2.34 g of diphenylphosphane−borane (11.7 mmol) in 7.0 mL of THF, 7.32 mL of 1.6 M *n*-butyllithium (11.7 mmol) in hexane, and 2.93 g of ditosylate **25** (4.88 mmol) in 9.0 mL of DMF. The crude product (3.7 g) was suspended in 20 mL of boiling ethanol and filtered off to give 3.18 g of **26** (99% based on **25**) as a colorless, nearly insoluble powder. Mp: 273 °C. $[\alpha]^{20}_D$: −34.9° (c = 0.045, $CHCl_3$). IR (KBr): 3052, 2878, 2411, 2389, 2354, 1436 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 0.6−1.6 (br s, 6), 2.35, 2.77 (2 d, 4, $|^2J|$ = 17.0 Hz), 2.94 (dd, 2, $|^2J|_{P,H}$ = 12.6 Hz, $|^2J|$ = 14.6 Hz), 3.23 (dd, 2, $|^2J|_{P,H}$ = 10.2 Hz), 3.83 (s, 2), 6.48 (m, 2), 6.81 (m, 2), 6.99 (m, 2), 7.32 (m, 2), 7.40−7.54 (m, 12), 7.72−7.80 (m, 8). Anal. Calcd for $C_{44}H_{44}P_2B_2$: C, 80.51; H, 6.76. Found: C, 80.23; H, 6.70.

(1*R*,2*R*,3*S*,4*S*)-1,2-Bis((diphenylphosphanyl)methyl)-3,4-diphenylcyclobutane (22). The whole procedure, work-up included, was conducted under an Ar atmosphere. To a solution of 1.40 g of **21** (2.21 mmol) in 20 mL of CH_2Cl_2 at room temperature was added 1.90 mL of HBF_4·OMe_2 (22.2 mmol) with a stainless steel cannula. Then, the mixture was heated at reflux for 6 h, while the liberated diborane was removed by an Ar stream at the top of the reflux condenser. After cooling to ambient temperature and careful neutralization with saturated, degassed $NaHCO_3$, the organic layer was taken with a syringe fitted with a stainless steel cannula. The aqueous layer was extracted twice with 20 mL of CH_2Cl_2. The combined organic phase was dried, filtered, and concentrated in vacuum to furnish 1.30 g of diphosphane **22** (97% based on **27**) as a colorless, foamy solid. Mp: 61 °C. $[\alpha]^{20}_D$: −17.4° (c = 0.77, $CHCl_3$). IR (KBr): 3052, 3026, 2919, 1600, 1584, 1433 cm^{-1}. MS (70 eV): m/z 604 $(M)^+$, 302 $(M/2)^+$. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 2.34 (m, 4), 2.48 (m, 2), 2.99 (half of AA′BB′ pattern, 2), 2.79 (m, 2), 7.02 (m, 4), 7.10−7.34 (m, 26). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 34.50 (d, $|^1J|_{P,C}$ = 12.2 Hz), 44.21 (t, $|^2J|_{P,C}$ = $|^3J|_{P,C}$ = 10.4 Hz), 53.37 (d, $|^3J|_{P,C}$ = 9.2 Hz), 126.16, 127.30, 128.14, 128.26, 128.35, 128.55, 132.55 (d, $|^2J|_{P,C}$ = 18.3 Hz), 133.06 (d, $|^2J|_{P,C}$ = 19.5 Hz), 138.35 (d, $|^1J|_{P,C}$ = 13.5 Hz), 138.85 (d, $|^1J|_{P,C}$ = 12.8 Hz), 142.52. ^{31}P-NMR (203 MHz, $CDCl_3$): δ −23.93. Anal. Calcd for $C_{42}H_{38}P_2$: C, 83.42; H, 6.33. Found: C 83.06, ; H, 6.24.

(1*S*,2*S*,6*S*,7*S*)-Dibenzo-1,6-bis((diphenylphosphanyl)-methyl)tricyclo[5.3.0.0^{2,6}]deca-3,8-diene (27). This compound was prepared in analogy to the procedure for **22** from 2.80 g of **26** (4.27 mmol) in 50 mL of CH_2Cl_2 and 5.20 mL of HBF_4·OMe_2 (42.7 mmol). The described workup procedure yielded 2.63 g of **27** as a colorless, foamy solid. On recrystallization from ethanol 2.48 g of diphosphane **27** (93% based on **26**) was obtained as colorless crystals. Mp: 112 °C. $[\alpha]^{20}_D$: −72.6° (c = 0.83, $CHCl_3$). IR (KBr): 3069, 3018, 2905, 1584, 1434 cm^{-1}. MS (70 eV): m/z 628 $(M)^+$, 314 $(M/2)^+$. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 2.53, 2.65 (2 d, 4, $|^2J|$ = 17.5 Hz), 2.71 (dd, 2, $|^2J|_{P,H}$ = 3.4 Hz, $|^2J|$ = 13.8 Hz), 2.91 (dd, 2, $|^2J|_{P,H}$ = 2.7 Hz), 3.55 (s, 2), 6.65 (m, 2), 6.88 (m, 2), 7.01 (m, 2), 7.04 (m, 2), 7.26−7.58 (m, 20). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 41.13 (d, $|^3J|_{P,C}$ = 9.8 Hz), 42.47 (d, $|^1J|_{P,C}$ = 15.8 Hz), 48.01 (d, $|^2J|_{P,C}$ = $|^3J|_{P,C}$ = 15.2 Hz), 60.38 (t, $|^3J|_{P,C}$ = 9.5 Hz), 124.02, 125.64, 125.75, 126.33, 128.41, 128.55 (d, $|^3J|_{P,C}$ = 8.6 Hz), 133.06 (d, $|^2J|_{P,C}$ = 19.5 Hz), 133.19 (d, $|^2J|_{P,C}$ = 20.1 Hz), 139.40 (d, $|^1J|_{P,C}$ = 12.8 Hz), 139.51 (d, $|^1J|_{P,C}$ = 13.4 Hz), 142.53, 145.05. ^{31}P-NMR (203 MHz, $CDCl_3$): δ −23.33. Anal. Calcd for $C_{44}H_{38}P_2$: C, 84.06; H, 6.09. Found: C, 83.74; H, 6.12.

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Supporting Information Available: An experimental section for compounds **10b**−**d**, **11b**−**d**, **12b**−**d**, **13b**−**d**, **14b**, **14c**, **15b**, **16b**, **17b**, and **18b** (8 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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