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Stereoselectivity of Michael Addition of P(X)−H-Type Nucleophiles to Cyclohexen-1-ylphosphine Oxide: The Case of Base-Selective Transformation

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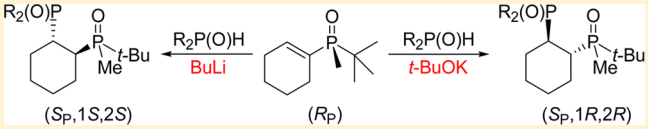
Supporting Information

ABSTRACT: Michael addition of phosphorus nucleophiles to the unsymmetrically substituted *tert*-butyl(1,4-cyclohexadien-3-yl)phosphine oxide and its derivatives has been described. The addition proceeds with the formation of the mixture of two isomeric products with good yield and diastereoselectivity.



The reaction of *tert*-butyl(cyclohexen-1-yl)methylphosphine oxide with phosphorus nucleophiles is base sensitive and might afford two epimers which differ at one chirality center. The absolute configuration of the products has been assigned on the basis of conformational and ^{1}H NMR analysis, and the mechanism of the reaction has been discussed. The Michael addition of phosphorus nucleophiles is postulated to proceed with or without consecutive epimerization of two α-carbanions.

INTRODUCTION

The design and synthesis of new chiral ligands has become one of the major goals in asymmetric synthesis. Chiral ligands possessing cyclohexyl linkers between two ligating centers are interesting targets where cyclohexane is responsible for the rigid arrangement of the molecule around the transition metal. This usually has a beneficial effect on the stereoselectivity of the asymmetric catalytic transformation. Among various ligands based on cyclic scaffolds, C_2-symmetric chiral 1,2-diaminocyclohexane-based ligands are particularly interesting.[1] The C_2-symmetry limits the number of possible coordination modes of the substrate to the catalyst. In addition, the 1,2-diaminocyclohexane framework could be easily modified, which allows the fast expansion of the ligand family. *trans*-1,2-Diaminocyclohexane is the well-known core structure for various chiral diamine or diimine ligands (Chart 1)[2] and also some *P*,*N*-ligands.[3] These ligands have been found to be effective chirality inductors in many asymmetric transformations such as the Henry reaction,[4] Michael addition,[5] or aldol reaction.[6] *trans*-Cyclohexane-1,2-diamine is also a useful (−)-sparteine surrogate,[7] and some derivatives have also been used as chiral auxiliaries in the preparation of chiral phosphonamides and their derivatives.[8]

Contrary to this, organophosphorus analogues of chiral *trans*-1,2-diaminocyclohexane have attracted little attention so far. There is only one report describing the synthesis and application of enantiomerically pure *C*-chiral *trans*-1,2-bis(phosphino)-cyclohexanes as ligands in asymmetric catalysis. Knochel et al. reported rhodium-catalyzed hydroboration−oxidation of styrene to (*S*)-1-phenylethanol in the presence of ligand **8** (Scheme 1).[9]

On the other hand, the preparation and application of some diphosphine ligands based on a rigid cyclopentane[10] and cyclobutane[11] backbone has been developed previously. The lack of data may be a consequence of difficulties in the synthesis of these ligands in enantiomerically pure form.

We have recently explored the dearomatization of the aryl groups in arylphosphines and their derivatives into the corresponding (1,4-cyclohexadien-3-yl)phosphine derivatives.[12,13] The structure of these products offers a possibility for profound modifications of the molecule using the reactivity of the isolated or conjugated double bonds or allyl anion.

In a recent communication from our laboratory, we reported the preparation of diphosphine dioxides possessing cyclohexenenyl linkers from secondary phosphine oxides and (1,4-cyclohexadien-3-yl)phosphine oxides (Scheme 2).[14]

Treatment of (1,4-cyclohexadien-3-yl)dimethylphosphine oxide (**10**) with secondary phosphine oxides in the presence of a base led to the formation of the product **12** with two phosphorus substituents in the 3 and 4 positions of the cyclohexene ring. The above result underlines the potential of phosphorylated Birch reduction products as substrates in the synthesis of cyclohexane-based diphosphine ligands.

Herein, we present our attempts in the preparation of the *P*,*C*-chiral *trans*-1,2-bis(phosphino)cyclohexane dioxides using Birch reduction−Michael addition sequence starting from unsymmetrically substituted aryldialkylphosphine oxide **14**.

RESULTS AND DISCUSSION

For test reactions, *rac*-*tert*-butylmethylphenylphosphine oxide (**14**) has been chosen (Scheme 3). This compound could be easily obtained in an optically pure form and used as precursor for Michael addition once the control experiments on racemate will confirm its synthetic utility. We assumed that the use of the enantiomerically pure organophosphorus compound with a stereogenic center already placed at the phosphorus atom would

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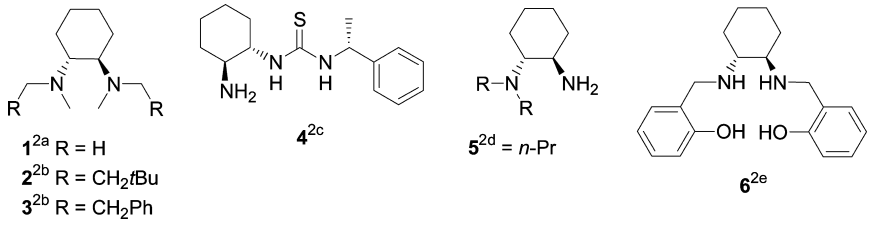
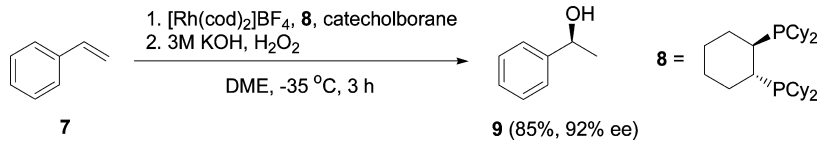
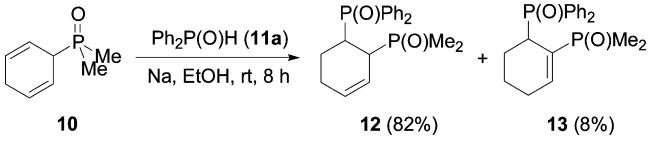
Chart 1. Chiral 1,2-Diaminocyclohexane-Based Ligands



Scheme 1. Asymmetric Hydroboration with 8



Scheme 2. Base-Induced Reaction between (1,4-Cyclohexadien-3-yl)phosphine Oxides and Secondary Phosphine Oxides



allow the synthesis of target diphosphine dioxides omitting the tedious racemate resolution step.

Starting *tert*-butyl(1,4-cyclohexadien-3-yl)methylphosphine oxide (**15**) was obtained through Birch reduction of the phosphine oxide **14** in an almost quantitative yield (Scheme 3).

In our previous observations, the best conversions in the Michael addition reaction of >P(O)H-type compounds to (1,4-cyclohexadien-3-yl)dimethylphosphine oxide were achieved using sodium ethoxide as the base. Based on this, we examined the reactivity of **15** with a variety of secondary phosphine oxides under the already developed reaction conditions (Table 1).

tert-Butyl(1,4-cyclohexadien-3-yl)methylphosphine oxide **15**, when subjected to the reaction with diphenylphosphine oxide **11a** in the presence of EtONa, afforded the corresponding Michael-type addition product **16a** accompanied by the isomeric adduct **17a**. Both the conversion of the substrate and the diastereoselectivity of the process were high. The *trans*-configuration of diphosphine dioxide **16** has been confirmed by 2D NMR analysis. With **11b**, compound **15** underwent a reaction affording a similar mixture of **16** and **17**. On the other hand, the use of the more sterically crowded secondary phosphine oxide **11c** led to the formation of compound **16c** as the practically sole reaction product along with complete diastereoselectivity. This suggests that the steric effects control both the diastereoselectivity of the addition and the eventual post-isomerization of the product. Among the tested secondary phosphine oxides, **11d** and **11e** failed to give the desired diphosphine dioxides (Table 1, entries 4 and 5). These two results are in sharp contrast with the results obtained recently by our research group,[14] and the most probable explanation is the steric effect induced by the presence of a *tert*-butyl group.

Scheme 3. Preparation of *tert*-Butyl(1,4-cyclohexadien-3-yl)methylphosphine Oxide (15)

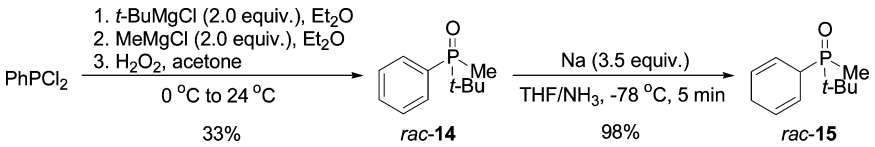
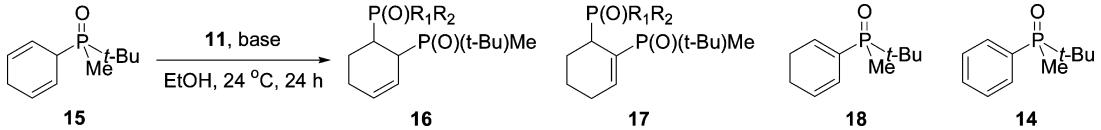


Table 1. Addition of >P(O)H-Type Compounds to *tert*-Butyl(1,4-cyclohexadien-3-yl)methylphosphine Oxide 15



				yield (%) (% de)[a]		
entry	>P(O)H-type compd		base (equiv)	16	17	18/14
1	**11a**	Ph	EtONa (10.0)	42 (82)	40 (80)	−/−
2	**11b**	*p*-An	EtONa (10.0)	38 (79)	31 (46)	11/5
3	**11c**	*o*-Tol	EtONa (10.0)	71 (100)	4 (100)[b]	traces/−
4	**11d**	Cy	NaH (1.1)[c]	4 (71)[d]	27 (100)[d]	−/55[d]
5	**11e**	*n*-Hex	NaH (1.1)[c]	0	0	−/100[d]

[a]Diastereomeric excess determined by ^{1}H NMR of the crude mixture. [b]The yield based on ^{1}H NMR of the isolated mixture of products. [c]1,4-Dioxane, 70 °C, 24 h. [d]Yield based on ^{1}H NMR of the crude mixture.

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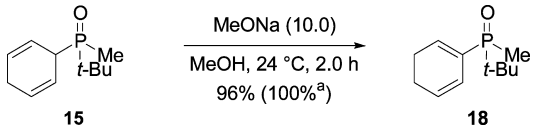
The addition of secondary phosphine oxides to **15** results in the formation of **16** along with the byproduct **17**. The synthesis of the desired cyclohexane-linked diphosphine ligands would therefore require hydrogenation of the double bond in **16** and **17**. Attempted hydrogenation of the Michael addition products revealed that **17** is resistant to C=C bond hydrogenation irrespective of the reaction conditions used.[15] Therefore, it is very important to optimize the Michael addition reaction toward the formation of compound **16**. Regarding this, our next attempt was the use of compound **18**, which could be obtained by isomerization of **15** (Scheme 4).

Scheme 4. Preparation of *tert*-Butyl(1,3-cyclohexadien-4-yl)methylphosphine Oxide (18)



Treatment of **15** with 10-fold excess of MeONa in methanol at room temperature for 2 h afforded cleanly the desired **18** in an almost quantitative yield. In the next step, this compound has been subjected to the reaction with a set of secondary phosphine oxides (Table 2).

tert-Butyl(1,3-cyclohexadien-2-yl)methylphosphine oxide **18** was found to undergo reaction with secondary phosphine oxides **11** under the same reaction conditions to furnish the corresponding Michael-type addition products **16** and **17**. In this case, however, the longer reaction time had a beneficial effect on both the conversion and diastereoselectivity (Table 2, entries 2, 3, 6, and 7).

The use of **18** in the Michael addition has again proceeded with the formation of the unwanted diphosphine dioxide **17**. In order to eliminate the possible isomerization of the double bond we decided to subject **18** to the selective hydrogenation of the nonconjugated double bond (Scheme 5).

Hydrogenation of **18** in the presence of Pd/C led to the formation of the compound **19** in excellent yield. The presence of only one double bond in the ring eliminates the formation of isomeric products which would make both purification and post-transformation far easier. Therefore, in the next step, compound **19** has been subjected to the optimization of Michael addition reaction with $Ph_2P(O)H$ (Table 3).

Scheme 5. Synthesis of 19

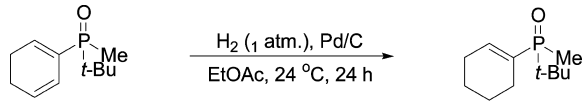
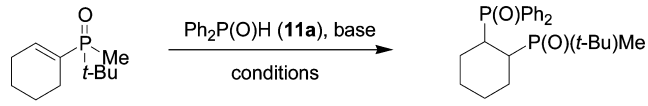


Table 3. Optimization of the Reaction between 19 and Diphenylphosphine Oxide 11a

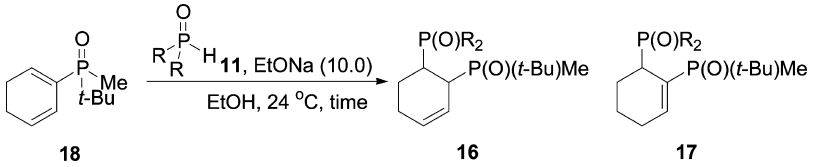


entry	base (equiv)	conditions	yield[a] (%)	% de[b]
1	EtONa (10.0)	EtOH, 24 °C, 24 h	0	
2	NaH (1.1)	1,4-dioxane, 70 °C, 24 h	0	
3	*n*-BuLi (1.0)	THF, 24 °C, 24 h	10	100
4	*n*-BuLi (1.0)	THF, 70 °C, 24 h	10	100
5	DBU (1.0)	THF, 70 °C, 20 h	4	−100
6	**LDA (1.0)**	**THF, 24 °C, 24 h**	**36 (57)**	**82**
7	*t*-BuOK (1.0)	THF, 24 °C, 24 h	57 (72)	−65
8	*t*-BuOK (1.0)	THF, 24 °C, 48 h	63 (65)	−61
9	*t*-BuOK (1.0)	THF, 60 °C, 24 h	34 (39)	−37
10	*t*-BuOK (1.0)	*t*-BuOH, 24 °C, 24 h	45 (50)	−100
11	*t*-BuOK (1.0)	*t*-BuOH, 80 °C, 24 h	49 (60)	−45
12	*t*-BuOK (1.0)	DMSO, 24 °C, 24 h	(21)	−100
13	*t*-BuOK (1.0)	DMSO, 60 °C, 24 h	0	
14	***t*-BuOK (1.0)**	**DMF, 24 °C, 24 h**	**79**	**-74**

[a]Yields based on ^{1}H NMR of the crude mixture are presented in parentheses. [b]Diastereomeric excess was determined by ^{1}H NMR of the crude mixture.

It appeared that the optimal conditions for Michael addition in the case of dienes **15** and **18** failed to yield the desired addition product **20a** similarly to the use of sodium hydride as a base in 1,4-dioxane (Table 3, entries 1 and 2). It seems that the presence of an additional conjugated double bond in **15** and **18** activates

Table 2. Michael Addition of 18



				yield (%) (% de)[a]	
entry	>P(O)H-type compd		time	**16**	**17**
1	**11a**	Ph	24 h	54 (87)	29 (83)
2	**11b**	*p*-An	18 h	39[b] (22)	25[b] (0)
3	**11b**	*p*-An	4d	52 (59)	34 (54)
4	**11c**	*o*-Tol	4d[c]	25 (100)	0
5	**11f**	1-Np	24 h	69 (100)	29 (100)
6	**11g**	*p*-Tol	18 h	58[b] (37)	40[b] (14)
7	**11g**	*p*-Tol	4d	57 (69)	31[d]

[a]Diastereomeric excess was determined by ^{1}H NMR of the crude mixture. [b]Yield based on ^{1}H NMR of the crude mixture. [c]After 18 h, traces of Michael addition product. [d]It was not possible to establish the de of the product.

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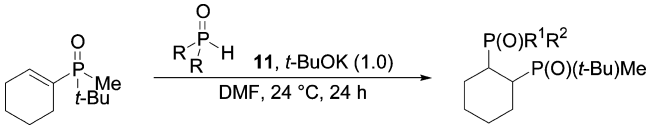
the substrate, thus enabling the addition of a nucleophile, which is not the case for **19**.

Therefore, a search for better reaction conditions has been undertaken. The use of *n*-BuLi as a base led to the desired **20a** but in a very low yield although with excellent diastereoselectivity (Table 3, entries 3 and 4). The use of DBU failed to produce the product in a reasonable amount (Table 3, entry 5), and the use of LDA led to the formation of the product with higher yield and with good diastereoselectivity (Table 3, entry 6). The best base, however, appeared to be *t*-BuOK, which allowed the preparation of the desired product in up to 79% yield and 74% de (Table 3, entry 14). Interestingly, the use of strong bases like LDA or *n*-BuLi led to the formation of Michael adducts with the opposite diastereoselectivity compared to DBU or *t*-BuOK. The possible explanation of this phenomenon will be discussed later in this paper.

With the newly optimized reaction conditions in hand, the addition of several secondary phosphine oxides **11** to **19** has been attempted (Table 4).

Table 4. Michael Addition of Secondary Phosphine Oxides to 19



entry	>P(O)H-type compd			yield[a] (%)	% de[b]
1	**11a**	Ph		79	−74
2	**11b**	*p*-An		58 (60)	−75
3	**11c**	*o*-Tol[c,d]		0	
4	**11d**	Cy[c,d]		0	
5	**11e**	*n*-Hex[c,d]		0	
6	**11f**	1-Np[c,d]		0	
7	**11g**	*p*-Tol[c,d]		61 (75)	−63
8	**11h**	Ph	*o*-An	81 (88)	−16

[a]Yields based on ^{1}H NMR of the crude mixture are presented in parentheses. [b]Diastereomeric excess was determined by ^{1}H NMR of the crude mixture. [c]DMF, 60 °C, 24 h. [d]Reaction performed at 24 °C failed to give the Michael addition products.

It appeared that the change of the structure of Michael acceptor influences the reactivity of the latter. Attempted reaction of more sterically crowded secondary phosphine oxides **11c** or **11f** failed to produce the desired diphosphine dioxide, which was not the case for **18** (Table 4, entries 3 and 6). For the less bulky phosphine oxides **11a**, **11b**, and **11g**, the reaction with **19** afforded the corresponding products with good yields and diastereomeric excess (Table 4, entries 1, 2, and 7). In one case, a reaction with unsymmetrically substituted Ph-*o*-AnP(O)H **11h** has been performed which yielded a mixture of only two epimers out of eight possible but with low diastereomeric excess (Table 4, entry 8).

As can be seen from Tables 1, 3, and 4, secondary phosphine oxides can undergo Michael addition reaction with either Birch reduction products or cyclohexenephosphine oxide derived from **14**. Regarding the availability of *P*-chiral nonracemic **14**, it was interesting to check out its utility in the synthesis of enantiomerically pure *P*-stereogenic diphosphine dioxides. The substrates for Michael addition were prepared from optically pure (R_P)-*tert*-butylphenylphosphine oxide **21** (Scheme 6).

(R_P)-**21** could be easily transformed into the corresponding (S_P)-**15**, (R_P)-**18** or (R_P)-**19** using alkylation with MeI/NaH followed by Birch reduction, isomerization, and hydrogenation of the nonconjugated double bond. The obtained compounds have been used in Michael addition with >P(X)H-type compounds (Scheme 7).

Addition of both $Ph_2P(O)H$ and *p*-$An_2P(O)H$ to (S_P)-**15** afforded a mixture of **16** and **17** in each case with the primary Michael adduct being the main reaction product. The diastereomeric excesses of **16a** and **16b** reached 87% de for **16a** and 79% de for **16b**, respectively. For both **16a** and **17a**, each diastereomer has been separated using column chromatography and then subjected to the conformational and NMR analysis using 1D and 2D NMR techniques.

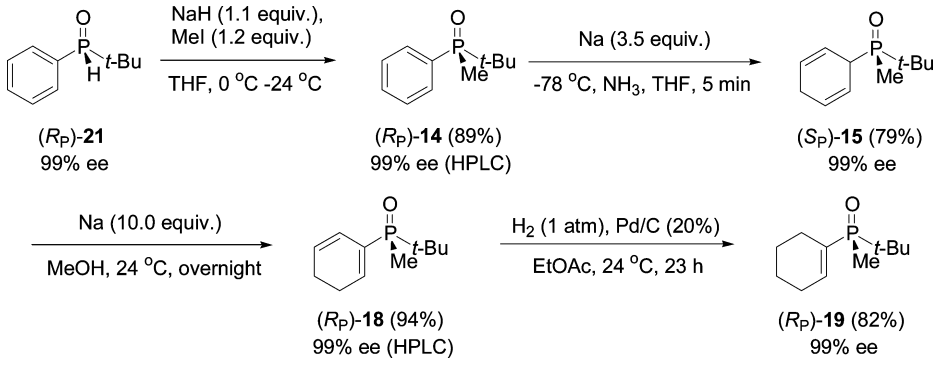
For **16**, two diastereomers are possible (Figure 1).

For each diastereomer, two conformers, diaxial and diequatorial, are possible. Regarding the structure of the adduct, the diaxial conformer should be more stable. A detailed conformational analysis revealed the presence of some interactions between the groups present at both phosphorus atoms (Figure 2).

For (S_P,3*R*,4*R*)-**16a**, there should be a slight shielding of the *tert*-butyl group by one of the phenyl groups from the $Ph_2P(O)$ moiety, and therefore, the signal should be shifted upfield in the ^{1}H NMR spectra (Figure 2). On the other hand, in (S_P,3*S*,4*S*)-**16a** there should be a shielding of methyl group by the carbon−phosphorus bond of the $Ph_2P(O)$ moiety, which should result in an upfield shift of the CH_3 signal (Figure 2). ^{1}H NMR analysis of both diastereomers revealed that the major diastereomer of **16a** possesses an S_P,3*R*,4*R* configuration at the chirality centers, whereas an S_P,3*S*,4*S* configuration has been assigned for the minor diastereomer.

Analogously, the conformational analysis has been performed for compound **17a** (Figure 3).

Scheme 6. Synthesis of (S_P)-15, (R_P)-18, and (R_P)-19



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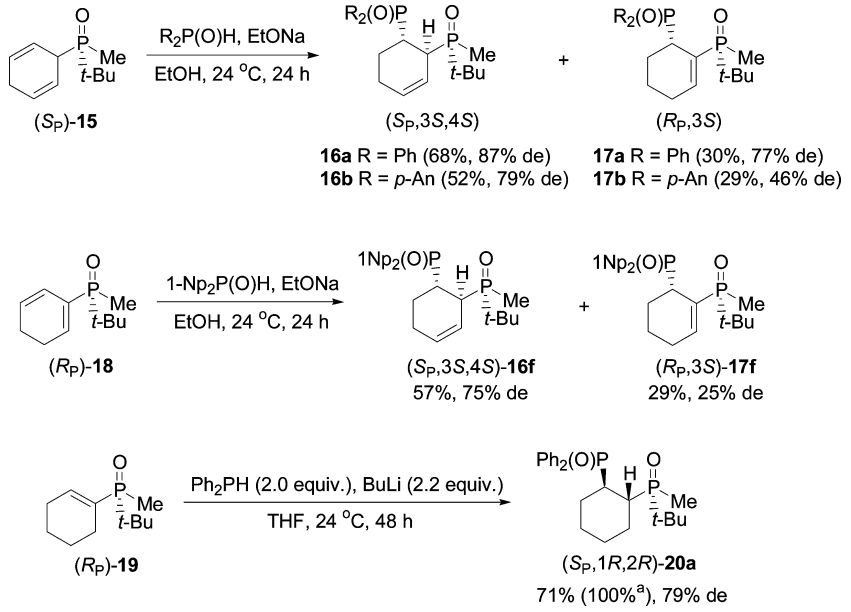
Scheme 7. Michael Addition Reactions of (S_P)-15, (R_P)-18, and (R_P)-19



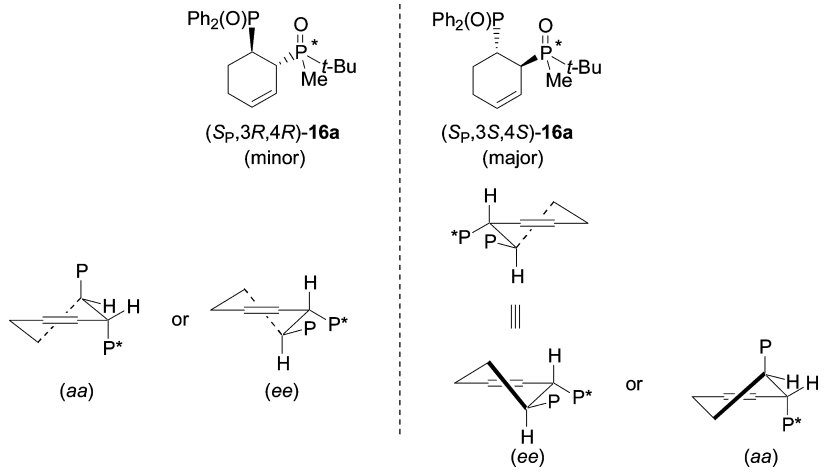


Figure 1. Conformations of (S_P,3*R*,4*R*)-**16a** and (S_P,3*S*,4*S*)-**16a**.

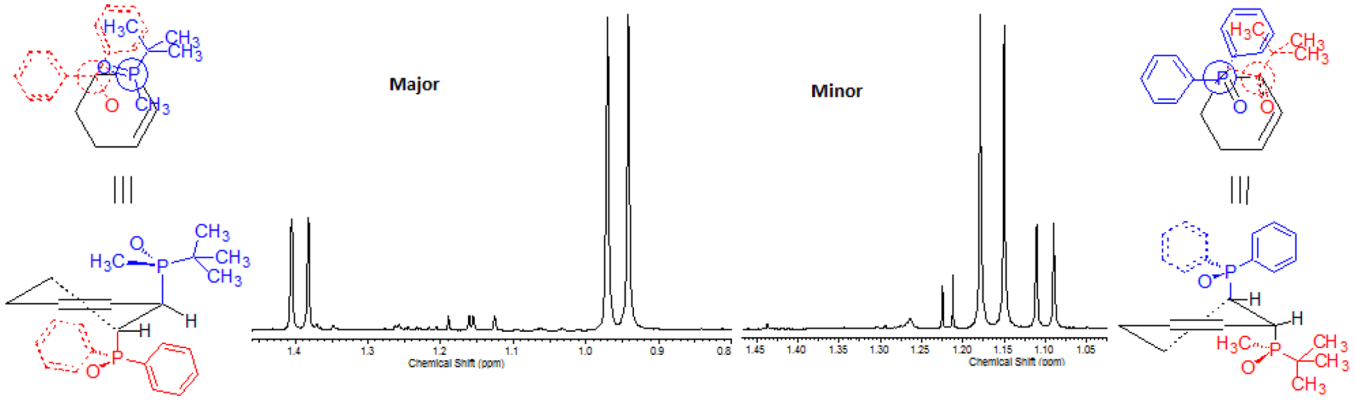


Figure 2. Newman projections of (S_P,3*S*,4*S*)-**16a** (left) and (S_P,3*R*,4*R*)-**16a** (right) along with partial ^{1}H NMR spectra.

The conformational analysis of (R_P,3*R*)-**17a** suggests some shielding of methyl group by one of the phenyl groups from the $Ph_2P(O)$ moiety, whereas for (R_P,3*S*)-**17a** some shielding of the *tert*-butyl group and, to a lesser degree, a shielding of CH_3 group by C═C bond is expected. ^{1}H NMR analysis of the pure diastereomers allowed the assignment of the absolute configuration for the major diastereomer of **17a** as R_P,3*S* and R_P,3*R* for the minor diastereomer.

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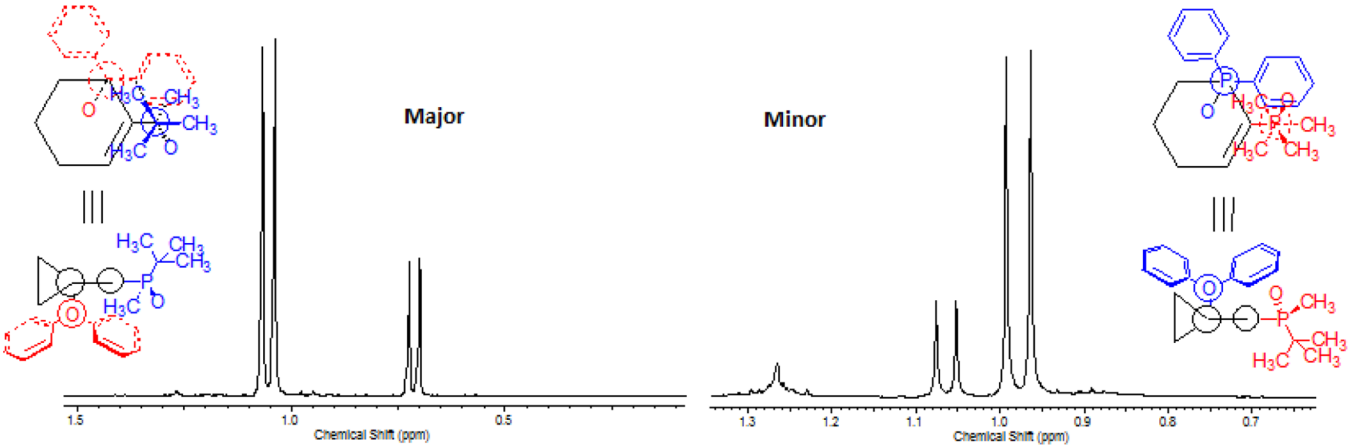
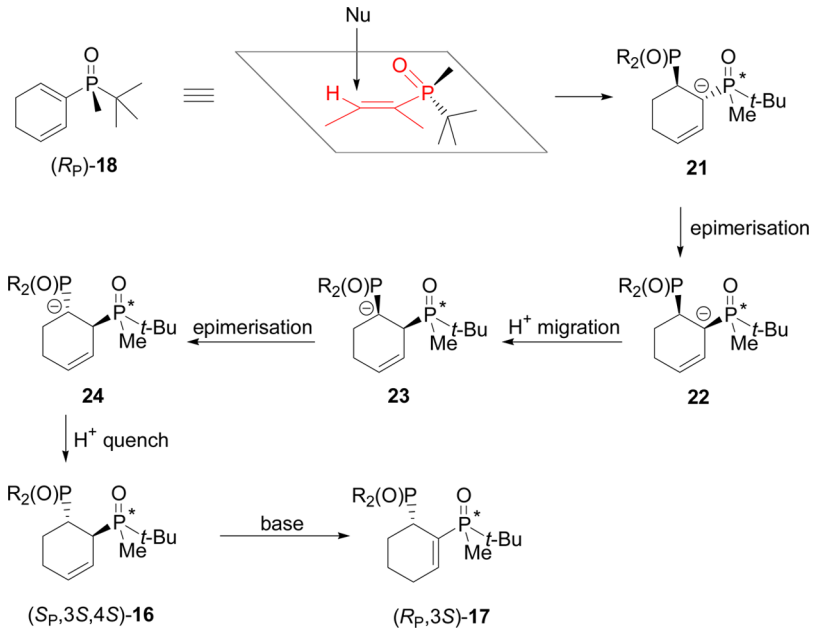


Figure 3. Newman projections of (R_P,3*S*)-**17a** (major, left) and (R_P,3*R*)-**17a** (minor, right) along with partial ^{1}H NMR spectra.

Scheme 8. Plausible Mechanism of the Formation of (S_P,3*S*,4*S*)-16a and (R_P,3*R*)-17a



Regarding the most stable conformation of the Michael acceptor,[16] the nucleophile should approach from the face opposite to the bulky *tert*-butyl group (Scheme 8).

This should lead to the formation of the intermediate **21** with *R* configuration at the carbon atom bonded to the $Ph_2P(O)$ group. The formation of (S_P,3*S*,4*S*)-**16a** must be therefore a consequence of the profound transformation of **21**. A conformational analysis of this carbanion revealed that, although *t*-BuMeP(O) group is placed in equatorial position, the bulky *tert*-butyl group is pointed under the cyclohexene ring in a pseudoaxial position (Figure 4).

To release the strain, the intermediate **21** must undergo the epimerization at C3, which leads to the carbanion **22** with an axial *t*-BuMeP(O) group and an equatorial $Ph_2P(O)$ group. This intermediate is rather unstable and would stabilize through proton migration from C4 to C3 to afford **23** followed by the second epimerization, which leads to the more conformationally stable intermediate **24** and, finally, diphosphine dioxide (S_P,3*S*,4*S*)-**16a**. This, in turn, can undergo double-bond migration under basic conditions to yield (R_P,3*S*)-**17a**.

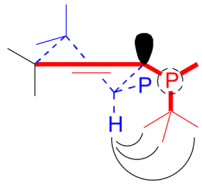


Figure 4. Interactions of *tert*-butyl group with cyclohexene ring in **21**.

The mechanism presented above suggests the crucial influence of the steric effects on the final outcome of the reaction. The presence of the bulky *tert*-butyl group induces the whole sequence of transformations leading from the less favorable diastereomer to the more energetically stable epimer.

A reaction between (R_P)-**19** and diphenylphosphine in the presence of *n*-BuLi led to the formation of **20a** as a mixture of two diastereomers but with high diastereomeric excess (Scheme 7). Similar to the reaction between racemic **19** and phosphine oxide **11a**, the use of *n*-BuLi led to the formation of the opposite diastereomer as the major product. Only the major diastereomer has been isolated and subjected to the conformational analysis (Figure 5).

The analysis revealed that, similar to **16a**, one of the epimers of **20a** should exhibit a shielding of the methyl group but to a lesser

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J. Org. Chem. XXXX, XXX, XXX−XXX

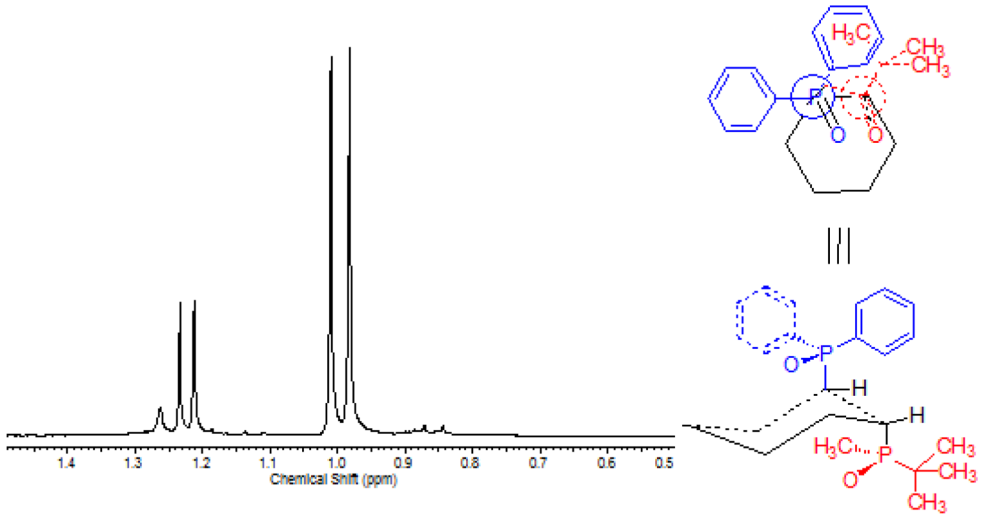

Figure 5. Newman projection of (S_P,1*R*,2*R*)-**20a** along with partial ^{1}H NMR spectra.

degree than in **16a** due to a slight conformational change of cyclohexyl ring. The other diastereomer should lack such interactions. ^{1}H NMR analysis revealed some shielding of the methyl group, which led to the assignment of the absolute configuration as (S_P,1*R*,2*R*)-**20a**.

The absolute configuration of (S_P,1*R*,2*R*)-**20a** has been confirmed using X-ray analysis of the crystals obtained by slow evaporation of DCM solution. The X-ray analysis confirmed also the diaxial arrangement of two phosphorus groups bonded to the cyclohexane framework, which suggests that in 1,2-disubstituted cyclohexane diaxial arrangement of two bulky group is more favorable than diequatorial arrangement. In this conformation, the interaction of two substituents must be substantially lower compared to the diequatorial conformation.

One of the interesting features was the base-dependent configuration of the Michael adducts. The use of organolithium bases led to the adduct while retaining the initial configuration at two new carbon centers, whereas with bases like EtONa or *t*-BuOK double epimerization has been observed. One of the possible explanations could be the formation of internal chelate between lithium cation and two phosphoryl oxygens, which should stabilize the initial configuration of the adduct (Figure 6).

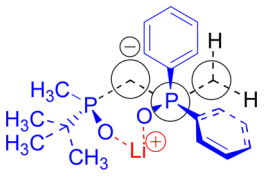

Figure 6. Possible stabilization of primary adduct by chelation of lithium cation.

Overall, the process described above is of practical interest as by a simple change of the base it is possible to control the configuration of the product, which could be used in the preparation of the matched/mismatched pairs of diphosphine ligands. This project is currently underway in our laboratory.

CONCLUSIONS

Michael addition of organophosphorus nucleophiles to α,β-unsaturated phosphine oxides has been a subject of numerous publications, but in the vast majority of cases the Michael acceptors possessed noncyclic character. The use of Michael acceptors with a double bond placed in the cyclic framework might have a serious impact on the stereochemical outcome of the addition reaction, especially when bulky substituents are placed in proximity to the reaction center. The results discussed above revealed an interesting feature of the tested Michael acceptors; namely, the absolute configuration of the product is base dependent. For bases like EtONa or *t*-BuOK, a rearrangement of the primary adduct has been observed through double epimerization of the α-carbanions, whereas for organolithium bases like *n*-BuLi or LDA the adduct retained the configuration in the adduct at newly formed chiral carbon atoms. This has been determined using both ^{1}H NMR analysis and conformational analysis. Such behavior might find application in the synthesis of match/mismatch pairs of diphosphine ligands for asymmetric catalysis.

EXPERIMENTAL SECTION

All reactions were performed under argon atmosphere using glassware vacuum- and flame-dried prior use. All reagents were purchased from commercial sources and used as received. Only dry solvents were used; ammonia was passed through a column filled with a solid potassium hydroxide before condensation. Solvents for chromatography and crystallization were distilled once before use, and solvents for extraction were used as received.

Analytics and Instruments. The NMR spectra were recorded on a 500 MHz spectrometer in $CDCl_3$ as solvent at room temperature unless otherwise noted. Chemical shifts (δ) are reported in ppm relative to residual solvent peak. Mass spectra were recorded in electron ionization (EI) mode, and GC was recorded using the following parameters: pressure 97.9 kPa, total flow 19.5 mL/min, column flow 1.5 mL/min, linear velocity 44.9 cm/s, split 10, temperature program (70 °C hold 3 min, 70−340 °C/12 °C/min hold 9.5 min, total 35 min). Thin-layer chromatography (TLC) was performed with precoated silica gel plates and visualized by UV light or $KMnO_4$ solution. The reaction mixtures were purified by column chromatography over silica gel (60−240 mesh). Enantiomeric purity of compounds was determined by HPLC analysis on a chiral stationary phase using 4.6 mm × 25 cm columns.

Diphenylphosphine oxide (**11a**),[17] bis-*p*-anisylphosphine oxide (**11b**),[17] bis-*o*-tolylphosphine oxide (**11c**),[17] di-*c*-hexylphosphine oxide (**11d**),[17] di-*n*-hexylphosphine oxide (**11e**),[18] bis-1-naphthylphosphine oxide (**11f**),[19] bis-*p*-tolylphosphine oxide (**11g**),[17] *o*-anisylphenylphosphine oxide (**11h**),[20] optically active (R_P)-*tert*-butylphenylphosphine oxide ((R_P)-**21**),[21] and optically active (R_P)-*tert*-butylphenylmethylphosphine

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J. Org. Chem. XXXX, XXX, XXX−XXX

oxide ((R_P)-**14**)[22] were synthesized according to reported procedures. Diphenylphosphine was commercially available and used as received.

*tert-Butylphenylmethylphosphine Oxide (**14**).* Into a flame-dried, three-necked, round-bottom flask (2000 mL) equipped with magnetic stirrer, reflux condenser, argon inlet, and a septum were placed magnesium (16.1 g, 0.67 mol) and one piece of iodine in 400 mL of dry degassed diethyl ether. Then, *t*-BuCl (73.42 mL, 0.67 mol) was added dropwise through a dropping funnel. *t*-BuCl (10%) was added to initiate the reaction, and after the reaction began the rest of the alkyl halide was added at a rate allowing gentle refluxing of the solvent. After addition of the halide, the mixture was stirred until all magnesium dissolved. Then, 600 mL of dry degassed diethyl ether was added, the Grignard solution was cooled to 0 °C, and $PhPCl_2$ (45.49 mL, 0.335 mol) in 300 mL of dry degassed diethyl ether was added dropwise by dropping funnel. The reaction mixture was allowed to warm to room temperature and stirred overnight under argon atmosphere. Then the reaction mixture was cooled to 0 °C, and solution of MeMgI in 400 mL of dry degassed diethyl ether prepared with the same procedure as *t*-BuMgCl was added dropwise via cannula. The reaction mixture was allowed to warm to room temperature and stirred overnight. The mixture was filtered and evaporated. The residue was dissolved in acetone and cooled to 0 °C. Then 15% H_2O_2 (200 mL) was added, and the mixture was stirred for 5 h. The mixture was diluted with water, the organic layer was removed, and the aqueous layer was washed with chloroform (5 × 100 mL). The organic fractions were collected, dried over anhydrous $MgSO_4$, filtered, and evaporated. The residue was purified by distillation under reduced pressure yielding 21.88 g (33%) of the title compound as a white solid: mp 59.3−60.4 °C; R_f 0.57 (CH_3Cl/MeOH, 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.13 (9H, d, J_{P-H} = 14.8 Hz), 1.72 (3H, d, J_{P-H} = 12.0 Hz), 7.44−7.55 (3H, m), 7.67−7.74 (2H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ 10.2 (d, J_{P-C} = 66.3 Hz), 24.2 (s), 32.5 (d, J_{P-C} = 70.8 Hz), 128.1 (d, J_{P-C} = 10.9 Hz), 131.46 (d, J_{P-C} = 8.2 Hz), 131.52 (d, J_{P-C} = 80.9 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 47.44 (s); GC t_R = 8.62 min; GC−MS (EI, 70 eV) m/z = 196 (M^+) (0.83), 140 (100), 125 (60), 77 (14), 47 (23). Anal. Calcd for $C_{11}H_{17}OP$: C, 67.33; H, 8.73. Found: C, 67.24; H, 8.65. Analytical data are in accordance with those reported in the literature.[23]

*tert-Butyl(1,4-cyclohexadien-3-yl)methylphosphine Oxide (**15**).* This compound was synthesized according to reported procedure[13] from *tert*-butylphenylmethylphosphine oxide (**14**) (0.600 g, 3.1 mmol) yielding 0.595 g (98%) of the title compound as a colorless pasty solid: R_f 0.18 (EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.16 (d, J_{P-H} = 14.2 Hz, 9H), 1.29 (d, J_{P-H} = 11.1 Hz, 3H), 2.60−2.76 (m, 2H), 3.38−3.56 (m, 1H), 5.66−5.96 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 7.2 (d, J_{P-C} = 63.8 Hz), 25.1 (s), 26.2 (d, J_{P-C} = 4.9 Hz), 39.0 (d, J_{P-C} = 59.5 Hz), 130.0 (d, J_{P-C} = 4.3 Hz), 127.0 (d, J_{P-C} = 8.9 Hz); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 58.50 (s); GC t_R = 11.10 min; GC−MS (EI, 70 eV) m/z = 140 (M^+) (3), 121 (7), 120 (100), 119 (7). Anal. Calcd for $C_{11}H_{19}OP$: C, 66.64; H, 9.66. Found: C, 66.80; H, 9.59.

General Procedure for One-Pot Reaction between *tert*-Butyl(1,4-Cyclohexadien-3-yl)methylphosphine Oxide (15) and >P(O)−H-Type Compounds (Method A). To a solution of secondary phosphine oxide **11** (0.5 mmol) in 1,4-dioxane or ethanol (3 mL) was added an appropriate amount of a base, and the reaction mixture was stirred at ambient temperature for 15 min. Subsequently, a solution of *tert*-butyl(1,4-cyclohexadien-3-yl)methylphosphine oxide (**15**) (0.099 g, 0.5 mmol) in 1,4-dioxane or ethanol (3 mL) was added, and the reaction mixture was heated at 70 °C or stirred at room temperature for 24 h. The reaction was then quenched by addition of saturated NH_4Cl solution (5 mL), diluted with water (5 mL), and extracted with diethyl ether (2 × 15 mL) and dichloromethane (2 × 15 mL). The collected organic phases were dried over $MgSO_4$, filtered, and evaporated to dryness under reduced pressure. The residue was purified by column chromatography (silica gel, $CHCl_3$/MeOH, 20:1).

*trans-3-(tert-Butylmethylphosphinoyl)-4-(diphenylphosphinoyl)-cyclohexene (**16a**).* This compound was prepared according to the general procedure (method A) from **15** (0.099 g, 0.5 mmol) and diphenylphosphine oxide (**11a**) (0.101 g, 0.5 mmol). Yield of two diastereoisomers 42% (82% de).

Major diastereoisomer: yield 0.076 g (38%); white solid; mp 174.3−175.3 °C; R_f 0.58 ($CHCl_3$/MeOH, 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.94 (d, J_{P-H} = 14.5 Hz, 9H), 1.38 (d, J_{P-H} = 11.4 Hz, 3H), 1.88−1.94 (m, 1H), 1.95−2.05 (m, 2H), 2.53−2.65 (m, 1H), 2.96−3.07 (m, 1H), 3.68−3.77 (m, 1H), 5.51−5.58 (m, 1H), 5.97−6.05 (m, 1H), 7.41−7.51 (m, 6H), 7.83−7.89 (m, 2H), 7.95−8.00 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 10.7 (d, J_{P-C} = 62.7 Hz), 19.5 (d, J_{P-C} = 2.7 Hz), 22.2 (dd, J_{P-C} = 2.5 Hz, J_{P-C} = 2.5 Hz), 24.1 (s), 28.7 (dd, J_{P-C} = 3.6 Hz, J_{P-C} = 70.8 Hz), 30.7 (d, J_{P-C} = 52.7 Hz), 32.9 (d, J_{P-C} = 65.4 Hz), 121.9 (d, J_{P-C} = 5.5 Hz), 128.6 (d, J_{P-C} = 16.4 Hz), 128.7 (d, J_{P-C} = 16.4 Hz), 130.7 (d, J_{P-C} = 10.0 Hz), 130.9 (d, J_{P-C} = 9.1 Hz), 131.47 (d, J_{P-C} = 8.2 Hz), 131.45 (dd, J_{P-C} = 2.7 Hz), 131.6 (d, J_{P-C} = 2.7 Hz), 132.1 (d, J_{P-C} = 94.7 Hz), 132.4 (d, J_{P-C} = 95.4 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 36.16 (d, J_{P-P} = 37.3 Hz), 55.43 (d, J_{P-P} = 37.3 Hz). GC t_R = 28.08 min; GC−MS (EI, 70 eV) m/z = 400 (M^+) (1.13), 282 (20), 281 (100), 204 (13), 203 (99), 202 (15), 201 (54), 200 (8), 199 (54), 186 (6), 185 (43), 183 (15), 155 (12), 154 (6), 153 (5), 152 (6), 143 (7), 141 (6), 128 (5), 125 (45), 123 (6), 121 (11), 119 (5), 103 (7), 95 (6), 80 (10), 79 (66), 78 (15), 77 (63), 65 (14), 63 (8), 57 (59), 51 (15), 47 (41), 41 (27), 39 (5), 29 (22). Anal. Calcd for $C_{23}H_{30}O_2P_2$: C, 68.99; H, 7.55. Found: C, 69.02; H, 7.56

Minor diastereoisomer: yield 0.008 g (4%); white solid; mp 182.4−183.1 °C; R_f 0.44 ($CHCl_3$/MeOH, 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.08 (d, J_{P-H} = 10.4 Hz, 3H), 1.15 (d, J_{P-H} = 14.5 Hz, 9H), 1.91−2.05 (m, 2H), 2.30−2.49 (m, 2H), 2.81−2.90 (m, 1H), 3.13−3.32 (m, 1H), 5.75−5.81 (m, 1H), 6.02−6.08 (m, 1H), 7.45−7.55 (m, 6H), 7.87−7.96 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 10.39 (d, J_{P-C} = 60.9 Hz), 19.40 (d, J_{P-C} = 2.6 Hz), 21.98 (dd, J_{P-C} = 1.8 Hz, J_{P-C} = 2.7 Hz), 25.26 (s), 31.26 (dd, J_{P-C} = 3.6 Hz, J_{P-C} = 69.0 Hz), 33.79 (d, J_{P-C} = 64.5 Hz), 34.33 (d, J_{P-C} = 54.5 Hz), 119.56 (d, J_{P-C} = 7.3 Hz), 128.62 (d, J_{P-C} = 3.9 Hz), 128.71 (d, J_{P-C} = 4.5 Hz), 131.17 (d, J_{P-C} = 8.2 Hz), 131.23 (d, J_{P-C} = 8.2 Hz), 131.30 (d, J_{P-C} = 94.5 Hz), 131.77 (d, J_{P-C} = 2.7 Hz), 132.50 (d, J_{P-C} = 94.5 Hz), ^{31}P NMR (202 MHz, $CDCl_3$) δ 34.28 (d, J_{P-P} = 39.8 Hz), 56.08 (d, J_{P-P} = 39.8 Hz). GC t_R = 26.26 min; GC−MS (EI, 70 eV) m/z = 400 (M^+) (6.43), 377 (5), 345 (5), 344 (19), 343 (15), 331 (8), 330 (19), 329 (86), 316 (6), 315 (7), 267 (11), 255 (6), 253 (23), 220 (6), 219 (19), 208 (5), 207 (17), 202 (6), 201 (31), 200 (10), 199 (100), 197 (9), 185 (8), 183 (16), 159 (10), 157 (8), 155 (8), 154 (8), 153 (5), 149 (5), 143 (15), 142 (9), 141 (19), 137 (6), 135 (9), 133 (5), 127 (5), 126 (7), 125 (16), 124 (7), 123 (8), 121 (7), 111 (6), 109 (7), 107 (6), 103 (6), 67 (5), 96 (5), 95 (7), 91 (14), 81 (9), 80 (7). Anal. Calcd for $C_{23}H_{30}O_2P_2$: C, 68.99; H, 7.55. Found: C, 68.97; H, 7.53.

*2-(tert-Butylmethylphosphinoyl)-3-(diphenylphosphinoyl)-cyclohexene (**17a**).* This compound was prepared according to the general procedure (method A) from **15** (0.099 g, 0.5 mmol) and diphenylphosphine oxide (**11a**) (0.101 g, 1.0 mmol): yield of two diastereoisomers 40% (80% de).

Major diastereoisomer: yield 0.072 g (36%); white solid; mp 242.7−243.2 °C; R_f 0.51 ($CHCl_3$/MeOH, 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.70 (d, J_{P-H} = 12.3 Hz, 3H), 1.03 (d, J_{P-H} = 14.2 Hz, 9H), 1.61−1.78 (m, 2H), 2.21−2.38 (m, 2H), 2.54−2.66 (m, 1H), 2.67−2.79 (m, 1H), 3.75−3.85 (m, 1H), 6.30−6.38 (m, 1H), 7.33−7.44 (m, 3H), 7.52−7.58 (m, 3H), 7.71−7.78 (m, 2H), 8.29−8.35 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 9.0 (d, J_{P-C} = 63.6 Hz), 18.3 (dd, J_{P-C} = 1.8 Hz, J_{P-C} = 1.8 Hz), 22.8 (dd, J_{P-C} = 3.1 Hz, J_{P-C} = 4.3 Hz), 24.2 (s), 25.1 (dd, J_{P-C} = 2.7 Hz, J_{P-C} = 12.7 Hz), 34.0 (d, J_{P-C} = 69.9 Hz), 37.0 (dd, J_{P-C} = 5.5 Hz, J_{P-C} = 66.3 Hz), 127.4 (d, J_{P-C} = 11.8 Hz), 128.4 (d, J_{P-C} = 10.9 Hz), 129.4 (dd, J_{P-C} = 6.7 Hz, J_{P-C} = 88.1 Hz), 131.1 (d, J_{P-C} = 2.7 Hz), 131.6 (d, J_{P-C} = 2.7 Hz), 132.2 (d, J_{P-C} = 9.1 Hz), 132.4 (d, J_{P-C} = 93.6 Hz), 132.8 (d, J_{P-C} = 9.1 Hz), 133.1 (d, J_{P-C} = 99.0 Hz), 143.1 (dd, J_{P-C} = 9.1 Hz, J_{P-C} = 9.1 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 35.09 (d, J_{P-P} = 5.0 Hz), 47.29 (d, J_{P-P} = 5.0 Hz). GC t_R = 26.31 min; GC−MS (EI, 70 eV) m/z = 400 (M^+) (7), 344 (20), 343 (12), 330 (15), 329 (76), 315 (5), 267 (11), 263 (5), 220 (6), 219 (23), 204 (5), 203 (5), 202 (7), 201 (30), 200 (14), 199 (100), 185 (8), 183 (20), 159 (11), 157 (8), 155 (7), 154 (5), 153 (5), 152 (6), 143 (17), 141 (25), 129 (5), 128 (5), 126 (5), 125 (16), 123 (9), 111 (7), 109 (7), 97 (6), 95 (9), 93 (5), 91 (7), 81 (14), 80 (7), 79 (53), 78 (13), 77 (58), 65 (14), 63 (15), 57 (36), 53 (5), 51 (15), 47 (27), 41 (30), 39 (6), 29 (25). Anal. Calcd for $C_{23}H_{30}O_2P_2$: C, 68.99; H, 7.55. Found: C, 68.99; H, 7.59

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J. Org. Chem. XXXX, XXX, XXX−XXX

Minor diastereoisomer: yield 0.008 g (4%); white solid; mp 212.3-213.2 °C; R_f 0.36 ($CHCl_3$/MeOH, 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.96 (d, J_{P-H} = 14.5 Hz, 9H), 1.05 (d, J_{P-H} = 12.0 Hz, 3H), 1.46−1.53 (m, 1H); 1.57−1.70 (m, 1H), 2.02−2.10 (m, 2H), 2.21−2.31 (m, 1H), 2.39−2.48 (m, 1H), 3.63−3.72 (m, 1H), 6.90−6.97 (m, 1H), 7.43−7.53 (m, 6H), 7.80−7.86 (m, 2H), 7.90−7.95 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 11.2 (d, J_{P-C} = 64.5 Hz), 17.8 (dd, J_{P-C} = 1.8 Hz, J_{P-C} = 4.5 Hz), 24.7 (s), 25.1 (dd, J_{P-C} = 4.5 Hz, J_{P-C} = 1.8 Hz), 25.4 (dd, J_{P-C} = 2.7 Hz, J_{P-C} = 11.8 Hz), 33.7 (d, J_{P-C} = 69.9 Hz), 36.7 (dd, J_{P-C} = 7.3 Hz, J_{P-C} = 66.3 Hz), 127.7 (dd, J_{P-C} = 6.4 Hz, J_{P-C} = 84.5 Hz), 128.3 (d, J_{P-C} = 11.8 Hz), 128.6 (d, J_{P-C} = 11.8 Hz), 131.2 (d, J_{P-C} = 9.1 Hz), 131.5 (d, J_{P-C} = 2.7 Hz), 131.7 (d, J_{P-C} = 2.7 Hz), 131.8 (d, J_{P-C} = 9.1 Hz), 133.1 (d, J_{P-C} = 94.5 Hz), 133.3 (d, J_{P-C} = 93.6 Hz), 149.3 (dd, J_{P-C} = 6.8 Hz, J_{P-C} = 7.3 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 31.39 (d, J_{P-P} = 5.0 Hz), 46.58 (d, J_{P-P} = 5.0 Hz). GC t_R = 27.43 min; GC−MS (EI, 70 eV) m/z = 400 (M^+) (2.21), 343 (11), 329 (37), 281 (18), 219 (12), 203 (21), 201 (29), 200 (13), 199 (100), 185 (13), 183 (17), 143 (14), 141 (14), 125 (19). Anal. Calcd for $C_{23}H_{30}O_2P_2$: C, 68.99; H, 7.55. Found: C, 68.96; H, 7.57.

*trans-3-(tert-Butylmethylphosphinoyl)-4-(di(p-anisyl)-phosphinoyl)cyclohexene (**16b**).* This compound was prepared according to the general procedure (method A) from **15** (0.099 g, 0.5 mmol) and bis-*p*-anisylphosphine oxide (**11b**) (0.131 g, 0.5 mmol). Yield of two diastereoisomers 38% (79% de).

Major diastereoisomer: yield 34% of title compound (0.032 g, 14% of pure compound and 20% containing 15% of **17b**) as a white solid; mp 139.6−141.2 °C; R_f 0.47 ($CHCl_3$/MeOH, 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.97 (d, J_{P-H} = 14.5 Hz, 9H), 1.37 (d, J_{P-H} = 11.4 Hz, 3H), 1.85−2.03 (m, 3H), 2.51−2.63 (m, 1H), 2.98−3.09 (m, 1H), 3.58−3.66 (m, 1H), 3.79 (s, 3H), 3.81 (s, 3H), 5.52−5.57 (m, 1H), 5.96−6.02 (m, 1H), 6.92−6.98 (m, 4H), 7.71−7.77 (m, 2H), 7.84−7.90 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 10.7 (d, J_{P-C} = 63.6 Hz), 19.5 (d, J_{P-C} = 2.5 Hz), 22.2 (dd, J_{P-C} = 1.9 Hz, J_{P-C} = 2.5 Hz), 24.1 (s), 29.0 (dd, J_{P-C} = 3.6 Hz, J_{P-C} = 71.8 Hz), 30.7 (d, J_{P-C} = 52.7 Hz), 32.8 (d, J_{P-C} = 65.4 Hz), 55.23 (s), 55.25 (s), 114.1 (d, J_{P-C} = 11.8 Hz), 114.2 (d, J_{P-C} = 12.7 Hz), 121.9 (d, J_{P-C} = 5.5 Hz), 123.6 (d, J_{P-C} = 101.7 Hz), 123.8 (d, J_{P-C} = 101.7 Hz), 130.6 (d, J_{P-C} = 10.9 Hz), 132.6 (d, J_{P-C} = 10.0 Hz), 133.2 (d, J_{P-C} = 9.1 Hz), 162.0 (d, J_{P-C} = 2.7 Hz), 162.1 (d, J_{P-C} = 2.7 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 36.60 (d, J_{P-P} = 37.3 Hz), 55.61 (d, J_{P-P} = 37.3 Hz). Anal. Calcd for $C_{25}H_{34}O_4P_2$: C 65.21, H 7.44. Found: C 65.28, H 7.47.

Minor diastereoisomer: yield 4% (as a mixture with **17b**) partially purified; colorless thick oil; R_f 0.45 ($CHCl_3$/MeOH, 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.11 (d, J_{P-H} = 10.4 Hz, 3H), 1.15 (d, J_{P-H} = 14.5 Hz, 9H), 1.88−2.02 (m, 2H), 2.35−2.45 (m, 1H), 2.82−2.93 (m, 1H), 3.04−3.14 (m, 1H), 3.81 (s, 3H), 3.82 (s, 3H), 5.73−5.80 (m, 1H), 5.98−6.04 (m, 1H), 6.95−6.99 (m, 4H), 7.73−7.84 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 10.5 (d, J_{P-C} = 60.9 Hz), 19.4 (d, J_{P-C} = 2.7 Hz), 21.9 (dd, J_{P-C} = 2.7 Hz, J_{P-C} = 2.7 Hz), 24.2 (s), 31.5 (dd, J_{P-C} = 3.6 Hz, J_{P-C} = 69.9 Hz), 33.7 (d, J_{P-C} = 64.5 Hz), 34.3 (d, J_{P-C} = 55.40 Hz), 55.25 (s), 55.25 (s), 114.1 (d, J_{P-C} = 9.1 Hz), 114.2 (d, J_{P-C} = 9.1 Hz), 119.7 (d, J_{P-C} = 7.3 Hz), 122.6 (d, J_{P-C} = 102.6 Hz), 123.8 (d, J_{P-C} = 101.7 Hz), 131.2 (d, J_{P-C} = 10.0 Hz), 132.9 (d, J_{P-C} = 9.4 Hz), 133.0 (d, J_{P-C} = 10.0 Hz), 162.15 (d, J_{P-C} = 2.7 Hz), 162.20 (d, J_{P-C} = 2.7 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 34.78 (d, J_{P-P} = 39.8 Hz), 56.37 (d, J_{P-P} = 39.8 Hz). Anal. Calcd for $C_{25}H_{34}O_4P_2$: C 65.21, H 7.44. Found: C 65.28, H 7.47.

*2-(tert-Butylmethylphosphinoyl)-3-(di(p-anisyl)phosphinoyl)-cyclohexene (**17b**).* This compound was prepared according to the general procedure (method A) from **15** (0.099 g, 0.5 mmol) and bis-*p*-anisylphosphine oxide (**11b**) (0.131 g, 0.5 mmol). Yield of two diastereoisomers 31% (74% de).

*Major diastereoisomer (3R)-**17b**:* yield 27%; isolated as a mixture with **16b** (both diastereomers) (24%); R_f 0.51 ($CHCl_3$/MeOH, 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.95 (d, J_{P-H} = 12.3 Hz, 3H), 1.03 (d, J_{P-H} = 14.2 Hz, 9H), 1.56−1.73 (m, 2H), 2.20−2.35 (m, 3H), 2.50−2.60 (m, 1H), 3.67−3.76 (m, 1H), 3.76 (s, 3H), 3.84 (s, 3H), 6.26−6.35 (m, 1H), 6.83−6.88 (m, 2H), 7.00−7.05 (m, 2H), 7.59−7.65 (m, 2H), 8.16−8.25 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 9.1 (d, J_{P-C} = 64.5 Hz), 18.3 (dd, J_{P-C} = 1.8 Hz, J_{P-C} = 1.8 Hz), 22.7 (dd, J_{P-C} = 2.3 Hz, J_{P-C} = 3.2 Hz), 24.2 (s), 25.0 (dd, J_{P-C} = 2.7 Hz, J_{P-C} = 12.7 Hz), 25.3 (d, J_{P-C} = 6.4 Hz), 33.9 (d, J_{P-C} = 69.9 Hz), 55.15 (s), 55.21 (s), 112.9 (d, J_{P-C} = 13.6 Hz), 113.9 (d, J_{P-C} = 12.7 Hz), 123.9 (d, J_{P-C} = 99.9 Hz), 124.9 (d, J_{P-C} = 106.3 Hz), 129.7 (dd, J_{P-C} = 6.3 Hz, J_{P-C} = 88.3 Hz), 133.9 (d, J_{P-C} = 10.0 Hz), 134.5 (d, J_{P-C} = 10.9 Hz), 142.7 (dd, J_{P-C} = 7.3 Hz, J_{P-C} = 7.3 Hz), 161.7 (d, J_{P-C} = 2.7 Hz), 162.1 (d, J_{P-C} = 2.7 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 35.15 (s), 47.39 (s).

Minor diastereoisomer: yield 0.009 g (4%); white solid; mp 70.0−70.3 °C; R_f 0.39 ($CHCl_3$/MeOH, 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.01 (d, J_{P-H} = 14.5 Hz, 9H), 1.06 (d, J_{P-H} = 12.0 Hz, 3H), 1.45−1.53 (m, 1H), 1.55−1.71 (m, 1H), 1.96−2.06 (m, 1H), 2.06−2.14 (m, 1H), 2.21−2.39 (m, 2H), 3.48−3.56 (m, 1H), 3.83 (s, 3H), 3.84 (s, 3H), 6.93−7.01 (m, 5H), 7.68−7.75 (m, 2H), 7.77−7.84 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 10.5 (d, J_{P-C} = 65.4 Hz), 17.7 (dd, J_{P-C} = 1.8 Hz, J_{P-C} = 4.5 Hz), 24.7 (s), 24.9 (dd, J_{P-C} = 2.0, Hz, J_{P-C} = 4.5 Hz), 25.3 (dd, J_{P-C} = 2.7 Hz, J_{P-C} = 11.8 Hz), 33.7 (d, J_{P-C} = 69.4 Hz), 37.6 (dd, J_{P-C} = 8.2 Hz, J_{P-C} = 68.1 Hz), 55.3 (s), 114.0 (d, J_{P-C} = 11.8 Hz), 114.2 (d, J_{P-C} = 11.8 Hz), 124.1 (d, J_{P-C} = 101.7 Hz), 124.3 (d, J_{P-C} = 99.9 Hz), 127.1 (d, J_{P-C} = 5.5 Hz), 127.8 (d, J_{P-C} = 5.5 Hz), 133.0 (d, J_{P-C} = 10.0 Hz), 133.6 (d, J_{P-C} = 10.0 Hz), 149.5 (dd, J_{P-C} = 6.4 Hz, J_{P-C} = 8.2 Hz), 162.2 (dd, J_{P-C} = 2.7 Hz, J_{P-C} = 22.7 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 31.69 (s), 46.75 (s). Anal. Calcd for $C_{25}H_{34}O_4P_2$: C, 65.21; H, 7.44. Found: C, 65.50; H, 7,58.

*trans-3-(tert-Butylmethylphosphinoyl)-4-(di(o-tolyl)-phosphinoyl)cyclohexene (**16c**).* This compound was prepared according to the general procedure (method A) from **15** (0.099 g, 0.5 mmol) and bis-*o*-tolylphosphine oxide (**11c**) (0.115 g, 0.5 mmol): yield 71% (0.133 g, 62% of pure compound and 9% containing about 4% of **17c** and 2% of **14**); colorless solid; mp 188.5−189.1 °C; R_f 0.57 ($CHCl_3$/MeOH, 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.15 (d, J_{P-H} = 14.5 Hz, 9H), 1.45 (d, J_{P-H} = 11.4 Hz, 3H), 1.76−1.86 (m, 1H), 1.92−2.12 (m, 2H), 2.24 (s, 3H), 2.33 (s, 3H), 2.41−2.53 (m, 1H), 3.25−3.37 (m, 1H), 3.97−4.05 (m, 1H), 5.60−5.67 (m, 1H), 5.96−6.03 (m, 1H), 7.12−7.17 (m, 2H), 7.25−7.37 (m, 3H), 7.38−7.42 (m, 1H), 8.02−8.13 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 11.0 (d, J_{P-C} = 64.5 Hz), 19.9 (d, J_{P-C} = 1.82 Hz), 21.1 (d, J_{P-C} = 4.5 Hz), 21.4 (d, J_{P-C} = 3.6 Hz), 22.0 (dd, J_{P-C} = 2.5 Hz, J_{P-C} = 1.8 Hz), 24.5 (s), 26.4 (dd, J_{P-C} = 2.7 Hz, J_{P-C} = 70.8 Hz), 31.6 (d, J_{P-C} = 52.7 Hz), 33.2 (d, J_{P-C} = 65.4 Hz), 122.1 (d, J_{P-C} = 6.4 Hz), 125.5 (d, J_{P-C} = 10.9 Hz), 125.6 (d, J_{P-C} = 10.9 Hz), 130.2 (d, J_{P-C} = 89.9 Hz), 130.3 (d, J_{P-C} = 10.9 Hz), 130.9 (d, J_{P-C} = 93.6 Hz), 131.57 (d, J_{P-C} = 9.1 Hz), 131.59 (d, J_{P-C} = 8.0 Hz), 131.7 (d, J_{P-C} = 10.9 Hz), 132.2 (d, J_{P-C} = 10.9 Hz), 132.4 (d, J_{P-C} = 10.0 Hz), 133.4 (d, J_{P-C} = 8.2 Hz), 140.9 (d, J_{P-C} = 6.8 Hz), 143.1 (d, J_{P-C} = 7.7 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 39.72 (d, J_{P-P} = 37.3 Hz), 56.18 (d, J_{P-P} = 37.3 Hz). GC t_R = 27.83 min; GC−MS (EI, 70 eV) m/z = 428 (M^+) (1), 310 (14), 309 (71), 253 (21), 232 (14), 231 (94), 230 (10), 229 (59), 215 (16), 213 (47), 211 (16), 207 (19), 200 (12), 199 (100), 197 (13), 196 (15), 179 (10), 165 (20), 139 (40), 137 (29), 135 (15), 133 (12), 121 (18), 109 (12), 91 (49). Anal. Calcd for $C_{25}H_{34}O_2P_2$: C, 70.08; H, 8.00. Found: C, 70.04; H, 8.03.

*2-(tert-Butylmethylphosphinoyl)-3-(di(o-tolyl)phosphinoyl)-cyclohexene (**17c**).* This compound was prepared according to the general procedure (method A) from **15** (0.099 g, 0.5 mmol) and bis-*o*-tolylphosphine oxide (**11c**) (0.115 g, 0.5 mmol) yielding 4% title compound containing about 9% of **16c** and 2% of **14**: R_f 0.41 ($CHCl_3$/MeOH, 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.69 (d, J_{P-H} = 12.0 Hz, 3H), 1,05 (d, J_{P-H} = 14.2 Hz, 9H), 1.51−1.60 (m, 1H), 1.92−2.02 (m, 2H), 2.26 (s, 3H), 2.28 (s, 3H), 2.53−2.66 (m, 2H), 2.81−2.90 (m, 1H), 4.13−4.21 (m, 1H), 6.57−6.64 (m, 1H), 7.10−7.16 (m, 1H), 7.17−7.22 (m, 2H), 7.25−7.35 (m, 2H), 7.37−7.41 (m, 1H), 7.72−7.77 (m, 1H), 7.85−7.91 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 9.2 (d, J_{P-C} = 63.6 Hz), 18.7 (dd, J_{P-C} = 1.9 Hz, J_{P-C} = 1.9 Hz), 23.0 (d, J_{P-C} = 3.6 Hz), 24.2 (s), 24.5 (s), 25.1 (dd, J_{P-C} = 2.7 Hz, J_{P-C} = 12.7 Hz), 33.2 (d, J_{P-C} = 69.5 Hz), 34.2 (d, J_{P-C} = 70.8 Hz), 124.8 (d, J_{P-C} = 12.7 Hz), 125.2 (d, J_{P-C} = 11.8 Hz), 128.1 (d, J_{P-C} = 10.9 Hz), 131.1 (d, J_{P-C} = 10.9 Hz), 131.5 (d, J_{P-C} = 8.2 Hz), 132.2 (d, J_{P-C} = 9.1 Hz), 134.9 (d, J_{P-C} = 10.0 Hz), 142.9 (d, J_{P-C} = 9.1 Hz), 143.3 (d, J_{P-C} = 6.4 Hz), 145.7 (dd, J_{P-C} = 8.2 Hz, J_{P-C} = 9.1 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 40.32 (d, J_{P-P} = 5.0 Hz), 46.89 (d, J_{P-P} = 5.0 Hz). GC t_R = 26.13 min; GC−MS (EI, 70 eV) m/z = 428 (M^+) (6), 413 (17), 371 (10), 357 (28), 229 (12), 213 (11),

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J. Org. Chem. XXXX, XXX, XXX−XXX

212 (24), 211 (10), 201 (14), 200 (15), 199 (100), 197 (12), 196 (12), 179 (19), 165 (15), 144 (13), 143 (16), 137 (18), 121 (11), 109 (13), 91 (37), 81 (12).

*trans-3-(tert-Butylmethylphosphinoyl)-4-(di(c-hexyl)-phosphinoyl)cyclohexene (**16d**).* This compound was prepared according to the general procedure (method A) from **15** (0.099 g, 0.5 mmol) and di-*c*-hexylphosphine oxide (**11d**) (0.107 g, 0.5 mmol): yield of two diastereoisomers based on ^{1}H NMR of the crude mixture 4%. Diastereomers were isolated as a complex mixture.

Major diastereoisomer: ^{31}P NMR (202 MHz, $CDCl_3$) δ 53.29 (d, J_{P-P} = 37.3 Hz), 60.38 (d, J_{P-P} = 37.3 Hz).

Minor diastereoisomer: ^{31}P NMR (202 MHz, $CDCl_3$) δ 55.17 (d, J_{P-P} = 39.8 Hz), 57.78 (d, J_{P-P} = 39.8 Hz).

*2-(tert-Butylmethylphosphinoyl)-3-(di(c-hexyl)phosphinoyl)-cyclohexene (**17d**).* This compound was prepared according to the general procedure (method A) from **15** (0.099 g, 0.5 mmol) and di-*c*-hexylphosphine oxide (**11d**) (0.107 g, 0.5 mmol): yield based on ^{1}H NMR of the crude mixture 27%; R_f 0.29 ($CHCl_3$/MeOH, 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.11 (d, J_{P-H} = 14.2 Hz, 9H), 1.19−1.32 (m, 7H), 1.40−1.49 (m, 2H), 1.50 (d, J_{P-H} = 11.7 Hz, 3H), 1.64−1.86 (m, 8H), 1.89−2.48 (m, 9H), 3.03−3.11 (m, 1H), 6.27−6.34 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 10.1 (d, J_{P-C} = 64.5 Hz), 18.3 (s), 23.8 (dd, J_{P-C} = 3.6 Hz, J_{P-C} = 4.5 Hz), 24.4 (s), 25.4 (dd, J_{P-C} = 1.8 Hz, J_{P-C} = 12.9 Hz), 25.5 (d, J_{P-C} = 4.5 Hz), 25.9 (d, J_{P-C} = 3.6 Hz), 26.1 (s), 26.2 (d, J_{P-C} = 2.7 Hz), 26.3 (s), 26.5 (d, J_{P-C} = 2.7 Hz), 26.6 (s), 26.7 (d, J_{P-C} = 2.7 Hz), 26.8 (d, J_{P-C} = 1.8 Hz), 26.9 (s), 32.4 (dd, J_{P-C} = 6.4 Hz, J_{P-C} = 52.7 Hz), 34.1 (d, J_{P-C} = 69.9 Hz), 36.1 (d, J_{P-C} = 60.9 Hz), 38.3 (d, J_{P-C} = 60.9 Hz), 130.9 (dd, J_{P-C} = 5.8 Hz, J_{P-C} = 87.9 Hz), 143.0 (dd, J_{P-C} = 7.3 Hz, J_{P-C} = 8.2 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 48.55 (s), 53.60 (s).

General Procedure for Synthesis of *tert*-Butyl(1,3-cyclohexadien-2-yl)methylphosphine Oxide (18) (Procedure B). A flame-dried Schlenk flask (25 mL) equipped with magnetic stirrer and argon inlet was placed in the water−ice bath. Dry ethanol (10 mL) and pieces of sodium (0.232 g, 0.010 mol) were then added. After dissolution of sodium (usually 20 min), a solution of *tert*-butyl(1,4-cyclohexadien-3-yl)methylphosphine oxide (**15**) (0.200 g, 1.01 mmol) in 5 mL of dry ethanol was added at once via syringe. The argon inlet was then replaced with an argon balloon, and the reaction mixture was stirred at room temperature for 2 h. Then NH_4Cl (satd) was added, and the mixture was extracted with DCM (3 × 30 mL). The organic layer was dried over $MgSO_4$, filtered, and evaporated. The residue was purified with column chromatography using $CHCl_3$/MeOH = 20:1 as eluent yielding 0.192 g (96%) of *tert*-butyl(1,3-cyclohexadien-2-yl)methylphosphine oxide (**18**): white solid; mp 45.4−47.1 °C; R_f 0.47 ($CHCl_3$/MeOH, 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.13 (d, J_{P-H} = 14.8 Hz, 9H), 1.49 (d, J_{P-H} = 12.0 Hz, 3H), 2.13−2.19 (m, 2H), 2.27−2.34 (m, 2H), 5.88−5.94 (m, 1H), 6.00−6.04 (m, 1H), 6.60−6.67 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 9.2 (d, J_{P-C} = 66.3 Hz), 21.1 (d, J_{P-C} = 1.8 Hz), 22.8 (d, J_{P-C} = 11.8 Hz), 24.3 (s), 32.4 (d, J_{P-C} = 71.8 Hz), 122.8 (d, J_{P-C} = 10.0 Hz), 127.0 (d, J_{P-C} = 10.0 Hz), 129.1 (d, J_{P-C} = 90.8 Hz), 139.4 (d, J_{P-C} = 4.5 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 45.94 (s). GC t_R = 12.05 min; GC−MS (EI, 70 eV) m/z = 198 (M^+) (18), 143 (8), 142 (100), 141 (17), 127 (44), 93 (17), 80 (18). Anal. Calcd for $C_{11}H_{19}OP$: C, 66.64; H, 9.66. Found: C, 66.69; H, 9.70.

One-Pot Reaction between *tert*-Butyl(1,3-Cyclohexadien-2-yl)methylphosphine Oxide (18) and >P(O)−H-Type Compounds. *trans-3-(tert-Butylmethylphosphinoyl)-4-(di(1-naphthyl)-phosphinoyl)cyclohexene (**16f**).* This compound was prepared according to the general procedure (method A) from *rac*-**18** (0.099 g, 0.5 mmol) and di-1-naphthylphosphine oxide (**11f**) (0.151 g, 0.5 mmol) yielding 69% (100% de) partially purified (0.092 g, 37%): white solid; mp 90.7−91.3 °C; R_f 0.49 ($CHCl_3$/acetone, 1:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.06 (d, J_{P-H} = 14.5 Hz, 9H), 1.43 (d, J_{P-H} = 11.7 Hz), 1.74−1.84 (m, 1H), 1.90−2.08 (m, 2H), 2.55−2.66 (m, 1H), 3.40−3.53 (m, 1H), 4.18−4.28 (m, 1H), 5.58−5.65 (m, 1H), 5.98−6.05 (m, 1H), 7.37−7.47 (m, 4H), 7.50−7.59 (m, 2H), 7.77−7.81 (m, 1H), 7.82−7.86 (m, 1H), 7.92−7.95 (m, 1H), 7.96−8.00 (m, 1H), 8.296−8.40 (m, 2H), 8.79−8.86 (m, 1H), 8.89−8.96 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 10.9 (d, J_{P-C} = 61.8 Hz), 20.1 (d, J_{P-C} = 1.8 Hz), 22.1 (dd, J_{P-C} = 2.7 Hz, J_{P-C} = 2.9 Hz), 24.3 (s), 28.7 (d, J_{P-C} = 69.9 Hz), 31.8 (d, J_{P-C} = 52.7 Hz), 33.1 (d, J_{P-C} = 64.5 Hz), 122.1 (d, J_{P-C} = 5.5 Hz), 124.58 (d, J_{P-C} = 12.7 Hz), 124.63 (d, J_{P-C} = 13.6 Hz), 126.2 (d, $_{P-C}$ = 6.4 Hz), 127.2 (d, J_{P-C} = 28.2 Hz), 128.5 (d, J_{P-C} = 90.8 Hz), 128.7 (s), 128.9 (s), 129.4 (d, J_{P-C} = 92.6 Hz), 130.4 (d, J_{P-C} = 10.9 Hz), 131.7 (d, J_{P-C} = 10.0 Hz), 132.9 (d, J_{P-C} = 2.7 Hz), 133.8 (d, J_{P-C} = 9.1 Hz), 134.0 (d, J_{P-C} = 8.2 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 42.33 (bm), 56.35 (d, J_{P-P} = 37.3 Hz). Anal. Calcd for $C_{31}H_{34}O_2P_2$: C, 74.38; H, 6.85. Found: C, 74.42; H, 6.89.

*2-(tert-Butylmethylphosphinoyl)-3-(di(1-naphthyl)phosphinoyl)-cyclohexene (**17f**).* This compound was prepared according to the general procedure (method A) from **18** (0.099 g, 0.5 mmol) and di-2-naphthylphosphine oxide (**11f**) (0.151 g, 0.5 mmol) yielding 29% of title compound partially purified (0.027g, 11%). Colorless pasty solid, R_f 0.56 ($CHCl_3$/Acetone, 1:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.16 (d, J_{P-H} = 12.3 Hz, 3H), 0.96 (d, J_{P-H} = 14.2 Hz, 9H), 1.66−1.74 (m, 1H), 1.80−1.98 (m, 1H), 2.33−2.43 (m, 1H), 2.47−2.58 (m, 1H), 2.81−2.92 (m, 1H), 2.92−3.04 (m, 1H), 4.13−4.23 (m, 1H), 6.32−6.42 (m, 1H), 7.25−7.30 (m, 1H), 7.37−7.43 (m, 1H), 7.44−7.56 (m, 4H), 7.63−7.68 (m, 1H), 7.82−7.87 (m, 1H), 7.88−7.92 (m, 2H), 8.07−8.11 (m, 1H), 8.39−8.46 (m, 1H), 8.94−8.99 (m, 1H), 9.36−9.40 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 7.8 (d, J_{P-C} = 64.5 Hz), 18.3 (s), 23.7 (dd, J_{P-C} = 2.7 Hz, J_{P-C} = 4.5 Hz), 24.3 (s), 25.2 (dd, J_{P-C} = 2.7 Hz, J_{P-C} = 11.8 Hz), 34.1 (d, J_{P-C} = 69.9 Hz), 36.1 (dd, J_{P-C} = 69.0 Hz, J_{P-C} = 6.4 Hz), 124.3 (d, J_{P-C} = 12.7 Hz), 124.8 (d, J_{P-C} = 14.5 Hz), 125.7 (s), 126.0 (s), 126.2 (s), 127.10 (s), 128.3 (s), 128.4 (d, J_{P-C} = 3.7 Hz), 128.5 (d, J_{P-C} = 1.2 Hz), 128.6 (d, J_{P-C} = 3.1 Hz), 128.7 (d, J_{P-C} = 1.2 Hz), 129.0 (d, J_{P-C} = 22.7 Hz), 129.5 (d, J_{P-C} = 43.6 Hz), 132.6 (d, J_{P-C} = 2.7 Hz), 133.1 (d, J_{P-C} = 2.7 Hz), 133.7 (d, J_{P-C} = 10.0 Hz), 134.0 (d, J_{P-C} = 7.3 Hz), 134.3 (d, J_{P-C} = 9.1 Hz), 134.4 (d, J_{P-C} = 12.7 Hz), 134.6 (d, J_{P-C} = 8.2 Hz), 145.4 (dd, J_{P-C} = 9.2 Hz, J_{P-C} = 9.2 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 45.35 (s),47.37 (s). Anal. Calcd for $C_{31}H_{34}O_2P_2$: C, 74.38; H, 6.85. Found: C, 74.44; H, 6.83.

*trans-3-(tert-Butylmethylphosphinoyl)-4-(di(p-tolyl)-phosphinoyl)cyclohexene (**16g**)* . This compound was prepared according to the general procedure (method A) from **18** (0.099 g, 0.5 mmol) and bis-*p*-tolylphosphine oxide (**11g**) (0.115 g, 0.5 mmol). Yield of two diastereoisomers 57% (69% de).

Major diastereoisomer: yield 49%, isolated as a mixture containing 7% of starting material and 17% of **17g**: R_f 0.38 ($CHCl_3$/acetone, 2:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.95 (d, J_{P-H} = 14.5 Hz, 9H), 1.37 (d, J_{P-H} = 11.4 Hz, 3H), 1.86−2.03 (m, 3H), 2.33 (s), 2.35 (s), 2.51−2.63 (m, 1H), 2.95−3.06 (m, 1H), 3.61−3.69 (m, 1H), 5.51−5.57 (m, 1H), 5.96−6.03 (m, 1H), 7.22−7.28 (m, 4H), 7.69−7.75 (m, 2H), 7.80−7.86 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 10.7 (d, J_{P-C} = 62.7 Hz), 19.5 (d, J_{P-C} = 2.7 Hz), 21.43 (s), 21.44 (s), 22.2 (dd, J_{P-C} = 2.7 Hz, J_{P-C} = 2.7 Hz), 24.1 (s), 28.8 (dd, J_{P-C} = 3.6 Hz, J_{P-C} = 70.8 Hz), 30.7 (d, J_{P-C} = 52.7 Hz), 32.8 (d, J_{P-C} = 65.4 Hz), 122.0 (d, J_{P-C} = 5.5 Hz), 129.2 (d, J_{P-C} = 98.1 Hz), 129.3 (d, J_{P-C} = 11.8 Hz), 129.4 (d, J_{P-C} = 10.9 Hz), 130.9 (d, J_{P-C} = 9.1 Hz), 131.4 (d, J_{P-C} = 8.2 Hz), 141.8 (dd, J_{P-C} = 2.7 Hz, J_{P-C} = 10.0 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 36.63 (d, J_{P-P} = 37.3 Hz), 55.42 (d, J_{P-P} = 37.3 Hz).

Minor diastereoisomer: yield 8%, isolated as a mixture containing 14% of **17g** (both diastereomers); R_f 0.22 ($CHCl_3$/acetone, 2:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.09 (d, J_{P-H} = 10.4 Hz, 3H), 1.15 (d, J_{P-H} = 14.5 Hz, 9H), 1.86−2.11 (m, 3 H), 2.36 (s, 3H), 2.38 (s, 3H), 2.53−2.61 (m, 1H), 2.81−2.91 (m, 1H), 3.07−3.14 (m, 1H), 5.74−5.81 (m, 1H), 5.99−6.07 (m, 1H), 7.21−7.30 (m, 4H), 7.65−7.72 (m, 2H), 7.72−7.80 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 10.4 (d, J_{P-C} = 60.9 Hz), 19.5 (d, J_{P-C} = 2.7 Hz), 21.5 (s), 22.0 (s), 25.3 (s), 31.4 (dd, J_{P-C} = 2.7 Hz, J_{P-C} = 69.9 Hz), 34.0 (d, J_{P-C} = 69.9 Hz), 34.2 (d, J_{P-C} = 56.3 Hz), 119.7 (d, J_{P-C} = 7.3 Hz), 128.2 (d, J_{P-C} = 97.2 Hz), 129.2 (d, J_{P-C} = 11.8 Hz), 129.3 (d, J_{P-C} = 11.8 Hz), 129.4 (d, J_{P-C} = 97.2 Hz), 131.1 (d, J_{P-C} = 8.2 Hz), 131.2 (d, J_{P-C} = 8.2 Hz), 131.8 (d, J_{P-C} = 9.1 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 34.66 (d, J_{P-P} = 39.8 Hz), 56.24 (d, J_{P-P} = 39.8 Hz).

*2-(tert-Butylmethylphosphinoyl)-3-(di(p-tolyl)phosphinoyl)-cyclohexene (**17g**)* . This compound was prepared according to the general procedure (method A) from **18** (0.099 g, 0.5 mmol) and

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J. Org. Chem. XXXX, XXX, XXX−XXX

bis-*p*-tolylphosphine oxide (**11g**) (0.115 g, 0.5 mmol). Yield of two diastereoisomers 31%.

Major diastereoisomer: yield 26%, isolated as a mixture containing 8% of **16g** and 5% of minor diastereomer; R_f 0.28 ($CHCl_3$/acetone, 2:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.73 (d, J_{P-H} = 12.3 Hz, 3H), 1.03 (d, J_{P-H} = 14.2 Hz, 9H), 1.60−1.71 (m, 2H), 1.86−2.05 (m, 1H), 2.24−2.36 (m, 2H), 2.31 (s), 2.40 (s), 2.63−2.73 (m, 1H), 3.72−3.80 (m, 1H), 6.30−6.38 (m, 1H), 7.13−7.18 (m, 2H), 7.30−7.35 (m, 2H), 7.59−7.65 (m, 2H), 8.09−8.18 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 9.1 (d, J_{P-C} = 64.5 Hz), 18.3 (dd, J_{P-C} = 1,8 Hz, J_{P-C} = 2.7 Hz), 21.5 (s), 22.8 (dd, J_{P-C} = 4.5 Hz, J_{P-C} = 2.7 Hz), 24.3 (s), 25.1 (dd, J_{P-C} = 2.7 Hz, J_{P-C} = 12.7 Hz), 29.6 (s), 36.8 (dd, J_{P-C} = 66.3 Hz, J_{P-C} = 5.4 Hz), 128.1 (d, J_{P-C} = 11.8 Hz), 130.1 (d, J_{P-C} = 73.6 Hz), 130.6 (d, J_{P-C} = 10.0 Hz), 132.0 (d, J_{P-C} = 9.1 Hz), 132.7 (d, J_{P-C} = 10.0 Hz), 141.2 (d, J_{P-C} = 2.7 Hz), 141.8 (d, J_{P-C} = 2.7 Hz), 143.0 (dd, J_{P-C} = 8.2 Hz, J_{P-C} = 9.1 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 35.17 (s), 46.98 (d, J_{P-P} = 5.0 Hz).

Minor diastereoisomer: yield 5%, isolated as a mixture containing 8% of **16g** and 9% of major diastereomer; R_f 0.09 ($CHCl_3$/acetone, 2:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.93−7.00 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 10.7 (d, J_{P-C} = 65.4 Hz), 17.8 (d, J_{P-C} = 2.7 Hz), 24.1 (s), 24.7 (s), 25.1 (d, J_{P-C} = 2.7 Hz), 25.4 (d, J_{P-C} = 1.8 Hz), 33.5 (d, J_{P-C} = 10.9 Hz), 37.6 (d, J_{P-C} = 8.2 Hz), 129.1 (d, J_{P-C} = 11.0 Hz), 130.2 (d, J_{P-C} = 3.6 Hz); 149.4 (dd, J_{P-C} = 5.5 Hz, J_{P-C} = 8.2 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 31.81 (s), 46.52 (s).

*tert-Butyl(cyclohexenyl)methylphosphine Oxide (**19**) (Procedure C).* A flame-dried round-bottom Schlenk-type flask with Rotaflo stopcock (50 mL) equipped with a magnetic stirrer and argon inlet was placed in the acetone−dry ice bath. A solution of *tert*-butyl(1,3-cyclohexadien-2-yl)methylphosphine oxide (**18**) (0.200 g, 1.01 mmol) in ethyl acetate (5 mL) was added, and solution was vacuum degassed. To the degassed solution was added an appropriate amount of palladium on carbon. The hydrogenation was performed at room temperature under hydrogen (1 atm) for 24 h. Then mixture was filtered through a thin layer of Celite and $MgSO_4$, which was rinsed with dichloromethane (4 × 5 mL) and evaporated to dryness. The residue was purified with column chromatography using $CHCl_3$/MeOH = 20:1 as eluent yielding 0.192 g (92%) of title compound as a colorless crystals: mp 49.4−52.0 °C; R_f 0.48 ($CHCl_3$/MeOH, 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.14 (d, J_{P-H} = 14.5 Hz, 9H), 1.46 (d, J_{P-H} = 12.0 Hz, 3H), 1.62−1.69 (m, 4H), 2.09−2.17 (m, 1H), 2.19−2.27 (m, 3H), 6.56−6.63 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 8.9 (d, J_{P-C} = 64.5 Hz), 21.5 (d, J_{P-C} = 1.8 Hz), 22.3 (d, J_{P-C} = 7.3 Hz), 24.4 (s), 26.2 (d, J_{P-C} = 12.7 Hz), 26.3 (d, J_{P-C} = 9.1 Hz), 32.6 (d, J_{P-C} = 70.0 Hz), 130.2 (d, J_{P-C} = 85.4 Hz), 142.5 (d, J_{P-C} = 5.5 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 48.23 (s). GC t_R = 7.65 min; GC−MS (EI, 70 eV) m/z = 200 (M^+) (7), 145 (9), 144 (100), 143 (12), 129 (57), 111 (8), 81 (25), 80 (9). Anal. Calcd for $C_{11}H_{21}OP$: C, 65.97; H, 10.57. Found: C, 66.00; H, 10.55.

One-Pot Reaction between *tert*-Butyl(cyclohexenyl)-methylphosphine Oxide (19) and >P(O)_H-Type Compounds. *trans-1-(tert-Butylmethylphosphinoyl)-2-(diphenylphosphinoyl)-cyclohexane **20a**.* This compound was prepared according to the general procedure (method A) from **19** (0.100 g, 0.5 mmol) and diphenylphosphine oxide (**11a**) (0.101 g, 0.5 mmol). Yield of two diastereoisomers 79% (74% de).

Major diastereoisomer: yield 0.133 g (66%); white solid; mp 39.0−40.0 °C; R_f 0.70 ($CHCl_3$/MeOH, 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.87 (d, J_{P-H} = 14.2 Hz, 9H), 1.42−1.59 (m, 2H), 1.56 (d, J_{P-H} = 11.7 Hz, 3H), 1.67−1.81 (m, 2H), 1.86−2.05 (m, 3H), 2.55−2.72 (m, 2H), 3.38−3.45 (m, 1H), 7.44−7.53 (m, 6H), 7.85−7.96 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 10.6 (d, J_{P-C} = 57.2 Hz), 21.5 (d, J_{P-C} = 1.8 Hz), 22.6 (s), 23.3 (d, J_{P-C} = 1.8 Hz), 24.1 (d, J_{P-C} = 1.8 Hz), 24.2 (s), 27.4 (d, J_{P-C} = 54.5 Hz), 30.6 (dd, J_{P-C} = 69.0 Hz, J_{P-C} = 2.7 Hz), 33.3 (d, J_{P-C} = 66.3 Hz), 128.6 (d, J_{P-C} = 10.9 Hz), 128.7 (d, J_{P-C} = 10.9 Hz), 131.0 (d, J_{P-C} = 9.1 Hz), 131.3 (d, J_{P-C} = 8.2 Hz), 131.45 (d, J_{P-C} = 2.7 Hz), 131.52 (d, J_{P-C} = 2.7 Hz), 132.2 (dd, J_{P-C} = 94.5 Hz, J_{P-C} = 1.8 Hz), 132.7 (d, J_{P-C} = 94.5 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 38.47 (d, J_{P-P} = 44.8 Hz), 58.72 (bs). GC t_R = 27.64 min; GC−MS (EI, 70 eV) m/z = 402 (M^+) (0.17), 284 (18), 283 (86), 202 (15), 203 (6), 201 (100), 183 (8), 155 (6), 145 (7), 125 (12), 119 (11), 81 (35). Anal. Calcd for $C_{23}H_{32}O_2P_2$: C, 68.64; H, 8.01. Found: C, 68.65; H, 7.98.

Minor diastereoisomer: yield 0.026 g (13%); white solid; mp 233.5−234.5 °C; R_f 0. 64 ($CHCl_3$/MeOH, 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.99 (d, J_{P-H} = 13.9 Hz, 9H), 1.22 (d, J_{P-H} = 10.7 Hz, 3H), 1.52−1.59 (m, 1H), 1.63−1.70 (m, 1H), 1.85−1.98 (m, 3H), 2.11−2.28 (m, 3H), 2.44−2.61 (m, 1H), 2.67−2.76 (m, 1H), 7.44−7.58 (m, 6H), 7.80−7.92 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 10.1 (d, J_{P-C} = 60.9 Hz), 22.0 (d, J_{P-C} = 1.9 Hz), 22.3 (d, J_{P-C} = 1.2 Hz), 23.2 (d, J_{P-C} = 2.7 Hz), 24.0 (d, J_{P-C} = 3.6 Hz), 24.7 (s), 29.7 (dd, J_{P-C} = 1.8 Hz, J_{P-C} = 57.2 Hz), 33.5 (d, J_{P-C} = 63.6 Hz), 33.8 (dd, J_{P-C} = 2.7 Hz, J_{P-C} = 67.2 Hz), 128.7 (d, J_{P-C} = 10.9 Hz), 128.8 (d, J_{P-C} = 10.9 Hz), 130.9 (d, J_{P-C} = 8.2 Hz), 131.0 (d, J_{P-C} = 8.2 Hz), 131.6 (dd, J_{P-C} = 2.7 Hz, J_{P-C} = 93.6 Hz), 131.7 (d, J_{P-C} = 2.7 Hz), 131.8 (d, J_{P-C} = 2.7 Hz), 132.8 (d, J_{P-C} = 93.6 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 36.18 (d, J_{P-P} = 49.8 Hz), 59.51 (d, J_{P-P} = 49.8 Hz). GC t_R = 22.28 min; GC−MS (EI, 70 eV) m/z = 284 (12), 283 (59), 202 (15), 201 (100), 183 (7), 155 (5), 145 (9), 125 (10), 119 (8), 81 (34). Anal. Calcd for $C_{23}H_{32}O_2P_2$: C, 68.64; H, 8.01. Found: C, 68.61; H, 8.00.

*trans-1-(tert-Butylmethylphosphinoyl)-2-(di(p-anisyl)-phosphinoyl)cyclohexene (**20b**).* This compound was prepared according to the general procedure (method A) from **19** (0.100 g, 0.5 mmol) and bis-*p*-anisylphosphine oxide (**11b**) (0.131 g, 0.5 mmol). Yield of two diastereoisomers 58% (75% de). Major diastereomer was isolated in pure form.

Major diastereoisomer: yield 51%, (44%, 0.102 g isolated as a pure compound, 7% isolated as a mixture containing 7% minor diastereomer and 16% of starting material) as a colorless solid; mp 43.6−45.2 °C; R_f 0.66 ($CHCl_3$/MeOH, 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88 (d, J_{P-H} = 13.9 Hz, 9H), 1.41−1.47 (m, 1H), 1.52 (d, J_{P-H} = 11.4 Hz, 3H), 1.61−1.78 (m, 2H), 1.81−2.00 (m, 3H), 2.50−2.68 (m, 3H), 3.26−3.33 (m, 1H), 3.79 (s, 3H), 3.82 (s, 3H), 6.94−6.97 (m, 4H), 7.71−7.76 (m, 2H), 7.78−7.83 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 10.6 (d, J_{P-C} = 57.2 Hz), 21,5 (d, J_{P-C} = 1.9 Hz), 22.7 (s), 23.4 (d, J_{P-C} = 1.8 Hz), 24.1 (d, J_{P-C} = 1.8 Hz), 24.3 (s), 27.5 (d, J_{P-C} = 55.4 Hz), 30.9 (dd, J_{P-C} = 69.9 Hz, J_{P-C} = 2.7 Hz), 33.2 (d, J_{P-C} = 66.3 Hz), 55.2 (s), 55.3 (s), 114.1 (d, J_{P-C} = 8.2 Hz), 114.2 (d, J_{P-C} = 8.2 Hz), 123.7 (dd, J_{P-C} = 1.8 Hz, J_{P-C} = 100.8 Hz), 124.3 (d, J_{P-C} = 101.7 Hz), 132.7 (d, J_{P-C} = 9.1 Hz), 133.1 (d, J_{P-C} = 10.0 Hz), 162.0 (d, J_{P-C} = 2.7 Hz), 162.1 (d, J_{P-C} = 3.2 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 38.80 (d, J_{P-P} = 44.8 Hz), 57.53 (d, J_{P-P} = 44.8 Hz). Anal. Calcd for $C_{25}H_{36}O_4P_2$: C, 64.92; H, 7.85. Found: C, 65.19; H, 8.03.

Minor diastereoisomer: yield 7% isolated as a mixture containing 7% of major diastereomer and 16% of starting material; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.03 (d, J_{P-H} = 13.9 Hz, 3H), 3.83 (s, 3H), 3.85 (s, 3H); ^{31}P NMR (202 MHz, $CDCl_3$) δ 36.44 (d, J_{P-P} = 49.8 Hz), 59.66 (d, J_{P-P} = 49.8 Hz).

*trans-1-(tert-Butylmethylphosphinoyl)-2-(di(p-tolyl)-phosphinoyl)cyclohexane (**20g**)* . This compound was prepared according to the general procedure (method A) from **19** (0.100 g, 0.5 mmol) and bis-*p*-tolylphosphine oxide (**11g**) (0.115 g, 0.5 mmol). Yield of two diastereoisomers 61% (63% de).

Major diastereoisomer: yield 0.105 g (49%); white solid; mp 187.2−187.6 °C; R_f 0.69 ($CHCl_3$/MeOH, 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.85 (d, J_{P-H} = 13.9 Hz, 9H), 1.39−1.55 (m, 2H), 1.51 (d, J_{P-H} = 11.4 Hz, 3H), 1.64−1.77 (m, 2H), 1.83−1.90 (m, 1H), 1.91−2.02 (m, 1H), 2.33 (s, 3H), 2.36 (s, 3H), 2.51−2.69 (m, 3H), 3.27−3.36 (m, 1H), 7.21−7.28 (m, 4H), 7.69−7.79 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 10.5 (d, J_{P-C} = 56.3 Hz), 21,4 (d, J_{P-C} = 1.2 Hz), 21.47 (d, J_{P-C} = 1.2 Hz), 21.52 (d, J_{P-C} = 1.9 Hz), 22.7 (s), 23.4 (d, J_{P-C} = 1.9 Hz), 24.16 (d, J_{P-C} = 2.1 Hz), 24.20 (s), 27.5 (d, J_{P-C} = 54.5 Hz), 30.8 (dd, J_{P-C} = 1.8 Hz, J_{P-C} = 70.0 Hz), 33.3 (d, J_{P-C} = 66.3 Hz), 129.1 (d, J_{P-C} = 97.2 Hz), 129.3 (d, J_{P-C} = 2.7 Hz), 129.4 (d, J_{P-C} = 2.7 Hz), 129.7 (d, J_{P-C} = 87.2 Hz), 131.0 (d, J_{P-C} = 9.1 Hz), 131.3 (d, J_{P-C} = 9.1 Hz), 141.8 (d, J_{P-C} = 2.7 Hz), 141.9 (d, J_{P-C} = 2.7 Hz); ^{31}P NMR (202 MHz, $CDCl_3$, 40 °C) δ 38.61 (d, J_{P-P} = 44.8 Hz), 57.33 (d, J_{P-P} = 44.8 Hz). GC t_R = 30.29 min; GC−MS (EI, 70 eV) m/z = 430 (M^+) (0.14), 312 (19), 311 (91), 230 (16), 229 (77), 202 (12), 201 (100), 145 (13), 139 (15), 119 (13), 91 (29), 81 (42). Anal. Calcd for $C_{25}H_{36}O_2P_2$: C, 69.75; H, 8.43. Found: C, 69,77; H, 8,46.

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J. Org. Chem. XXXX, XXX, XXX−XXX

Minor diastereoisomer: yield 0.026 g (12%); white solid; mp 69.9−70.6 °C; R_f 0.64 ($CHCl_3$/MeOH, 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.00 (d, J_{P-H} = 13.9 Hz, 9H), 1.22 (d, J_{P-H} = 10.7 Hz, 3H), 1.24−1.27 (m, 1H), 1.51−1.57 (m, 1H), 1.64−1.69 (m, 1H), 1.83−1.96 (m, 3H), 2.10−2.17 (m, 1H), 2.19−2.27 (m, 1H), 2.36 (s, 3H), 2.40 (s, 3H), 2.43−2.59 (m, 1H), 2.61−2.69 (m, 1H), 7.25−7.28 (m, 2H), 7.29−7.33 (m, 2H), 7.67−7.77 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 10.1 (d, J_{P-C} = 60.9 Hz), 21.5 (d, J_{P-C} = 1.8 Hz), 21.5 (d, J_{P-C} = 1.2 Hz), 22.0 (d, J_{P-C} = 1.8 Hz), 22.3 (d, J_{P-C} = 1.2 Hz), 23.2 (d, J_{P-C} = 1.8 Hz), 24.0 (d, J_{P-C} = 4.5 Hz), 24.7 (s), 29.6 (dd, J_{P-C} = 1.8 Hz, J_{P-C} = 57.2 Hz), 33.5 (d, J_{P-C} = 63.6 Hz), 33.9 (dd, J_{P-C} = 2.7 Hz, J_{P-C} = 68.1 Hz), 128.5 (dd, J_{P-C} = 2.7 Hz, J_{P-C} = 97.2 Hz), 129.4 (d, J_{P-C} = 11.8 Hz), 129.5 (d, J_{P-C} = 10.9 Hz), 129.6 (d, J_{P-C} = 96.3 Hz), 130.8 (d, J_{P-C} = 9.1 Hz), 131.0 (d, J_{P-C} = 9.1 Hz), 142.1 (d, J_{P-C} = 2.7 Hz), 142.2 (d, J_{P-C} = 2.7 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 36.62 (d, J_{P-P} = 49.8 Hz), 59.40 (d, J_{P-P} = 49.8 Hz). GC t_R = 30.19 min; GC−MS (EI, 70 eV) m/z = 430 (M^+) (0.36), 312 (17), 311 (88), 230 (15), 229 (84), 202 (11), 201 (100), 145 (14), 139 (24), 121 (11), 119 (14), 92 (12), 91 (39), 81 (46). Anal. Calcd for $C_{25}H_{36}O_2P_2$: C, 69.75; H, 8.43. Found: C, 69,79; H, 8,40.

*trans-1-(tert-Butylmethylphosphinoyl)-2-(o-anisylphenylphosphinoyl)cyclohexane (**20h**).* This compound was prepared according to the general procedure (method A) from **19** (0.100 g, 0.5 mmol) and *o*-anisylphenylphosphine oxide (**11h**) (0.116 g, 0.5 mmol). Yield of two diastereoisomers 81% (16% de).

Major diastereoisomer: yield 51%, isolated as a mixture containing 30% of minor diastereomer; R_f 0.73 ($CHCl_3$/MeOH, 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.85 (d, J_{P-H} = 13.9 Hz, 9H), 1.45−1.51 (m, 1H), 1.52 (d, J_{P-H} = 11.7 Hz, 3H), 1.61−1.91 (m, 3H), 1.92−2.06 (m, 2H), 2.37−2.47 (m, 1H), 2.55−2.80 (m, 1H), 2.37−2.46 (m, 1H), 3.68−3.75 (m, 1H), 3.81 (s, 3H), 6.79−6.82 (m, 1H), 7.09−7.14 (m, 1H), 7.38−7.51 (m, 4H), 7.97−8.02 (m, 2H), 8.15−8.19 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 10.5 (d, J_{P-C} = 56.3 Hz), 21.6 (s), 22.7 (s), 23.3 (s), 24.1 (s), 24.3 (s), 28.0 (d, J_{P-C} = 56.3 Hz), 29.5 (dd, J_{P-C} = 69.9 Hz, J_{P-C} = 2.7 Hz), 33.3 (d, J_{P-C} = 66.3 Hz), 54.9 (s), 110.6 (d, J_{P-C} = 6.4 Hz), 120.5 (d, J_{P-C} = 91.7 Hz), 120.9 (d, J_{P-C} = 10.9 Hz), 127.9 (d, J_{P-C} = 11.8 Hz), 131.1 (d, J_{P-C} = 2.7 Hz), 131.9 (d, J_{P-C} = 9.1 Hz), 132.4 (d, J_{P-C} = 95.4 Hz), 133.8 (d, J_{P-C} = 135.0 (d, J_{P-C} = 4.5 Hz), 159.4 (d, J_{P-C} = 4.5 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 38.14 (d, J_{P-P} = 49.8 Hz), 57.97 (d, J_{P-P} = 49.8 Hz); GC t_R = 28.37 min GC−MS (70 eV, EI) m/z = 432 (M^+) (0.15), 355 (30), 314 (21), 313 (100), 231 (24), 201 (68), 199 (30), 152 (14), 145 (12), 137 (11), 119 (14), 91 (59), 81 (38).

Minor diastereoisomer: yield 30%, isolated as a mixture containing 51% of major diastereomer; R_f 0.73 ($CHCl_3$/MeOH, 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.91 (d, J_{P-H} = 13.9 Hz, 9H), 1.45−1.51 (m, 1H), 1.55 (d, J_{P-H} = 12.0 Hz, 3H), 1.61−1.91 (m, 3H), 1.92−2.06 (m, 2H), 2.37−2.47 (m, 1H), 2.55−2.80 (m, 1H), 3.82−3.88 (m, 1H), 3.87 (s, 3H), 6.87−6.90 (m, 1H), 7.09−7.14 (m, 1H), 7.38−7.51 (m, 4H), 8.01−8.06 (m, 2H), 8.12−8.18 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 10.6 (d, J_{P-C} = 58.1 Hz), 21.8 (s), 22.7 (s), 23.6 (s), 24.4 (s), 27.5 (d, J_{P-C} = 56.3 Hz), 29.7 (dd, J_{P-C} = 69.9 Hz, J_{P-C} = 2.7 Hz), 33.4 (d, J_{P-C} = 65.4 Hz), 55.3 (s), 110.5 (d, J_{P-C} = 7.3 Hz), 121.2 (d, J_{P-C} = 10.9 Hz), 128.2 (d, J_{P-C} = 11.8 Hz), 131.3 (d, J_{P-C} = 2.7 Hz), 131.7 (d, J_{P-C} = 9.1 Hz), 133.4 (d, J_{P-C} = 96.3 Hz), 133.7 (d, J_{P-C} = 1.8 Hz), 134.5 (d, J_{P-C} = 4.5 Hz), 159.1 (d, J_{P-C} = 4.5 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 39.44 (d, J_{P-P} = 47.3 Hz), 57.97 (d, J_{P-P} = 47.3 Hz); GC t_R = 28.59 min GC−MS (70 eV, EI) m/z = 432 (M^+) (0.12), 314 (21), 313 (100), 231 (22), 201 (59), 199 (25), 152 (10), 119 (12), 91 (47), 81 (33).

*(R_P)-tert-Butylphenylmethylphosphine Oxide ((R_P)-**14**).* This compound was synthesized according to reported procedure[22] from (R_P)-(**21**) (0.600 g, 3.3 mmol, >99.5% ee) yielding 0.578 g (89%) of title compound: $[\alpha]_D$ = +21.4 (*c* 1.10, MeOH) (lit.[24] $[\alpha]_D$ = +22.7 (*c* 1.0, MeOH)); HPLC (Chiralcel OD-H, hexane/*i*-PrOH = 98.5:1.5, 1 mL/min, *t* = 80 min) t_R = 43.40 min (100% ee).

*(S_P)-tert-Butyl(1,4-cyclohexadien-3-yl)methylphosphine Oxide ((S_P)-**15**).* This compound was synthesized according to reported procedure[13] from (R_P)-(**14**) (0.099 g, 0.5 mmol) yielding 0.08 g (79%) of title compound.

*(R_P)-tert-Butyl(1,3-cyclohexadien-2-yl)methylphosphine Oxide ((R_P)-**18**).* This compound was synthesized according to procedure B from (S_P)-(**15**) (0.040 g, 0.2 mmol) yielding 0.037 g (94%) of title compound: HPLC (Chiralcel OD-H, Hexane/*i*-PrOH = 98.5:1.5, 1 mL/min, *t* = 80 min) t_R = 32.50 min (>99.5% ee).

*(R_P)-tert-Butyl(cyclohexenyl)methylphosphine Oxide ((R_P)-**19**).* This compound was synthesized according to procedure C from (R_P)-(**18**) (0.100 g, 0.5 mmol) yielding 0.083 g (82%) of title compound.

*(S_P,3S,4S)-3-(tert-Butylmethylphosphinoyl)-4-(diphenylphosphinoyl)cyclohexene ((S_P,3S,4S)-**16a**).* This compound was prepared according to the general procedure (method A) from (S_P)-**15** (0.200 g, 1.0 mmol) and diphenylphosphine oxide (**11a**) (0.204 g, 1.0 mmol) yielding 0.238 g (59%) of title compound: $[\alpha]_D$ = +10.3 (*c* 1.01, MeOH).

*(S_P,3R,4R)-3-(tert-Butylmethylphosphinoyl)-4-(diphenylphosphinoyl)cyclohexene ((S_P,3R,4R)-**16a**).* This compound was prepared according to the general procedure (method A) from (S_P)-**15** (0.200 g, 1.0 mmol) and diphenylphosphine oxide (**11a**) (0.204 g, 1.0 mmol) yielding 0.036 g (9%) of title compound: $[\alpha]_D$ = −72.2 (*c* 0.50, MeOH).

*(S_P,3S,4S)-3-(tert-Butylmethylphosphinoyl)-4-(di(p-anisyl)-phosphinoyl)cyclohexene ((S_P,3S,4S)-**16b**)* . This compound was prepared according to the general procedure (method A) from (S_P)-**15** (0.580 g, 2.9 mmol) and bis-*p*-anisylphosphine oxide (**11b**) (0.768 g, 2.9 mmol) yielding 47% of title compound containing 24% of (R_P,3S)-**17b**.

*(S_P,3R,4R)-2-(tert-Butylmethylphosphinoyl)-3-(di(p-anisyl)-phosphinoyl)cyclohexene ((S_P,3R,4R)-**16b**)* . This compound was prepared according to the general procedure (method A) from (S_P)-**15** (0.580 g, 2.9 mmol) and bis-*p*-anisylphosphine oxide (**11b**) (0.768 g, 2.9 mmol) yielding 5% of title compound containing 1% of (R_P,3S)-**17b**.

*(S_P,3S,4S)-3-(tert-Butylmethylphosphinoyl)-4-(di(1-naphthyl)-phosphinoyl)cyclohexene ((S_P,3S,4S)- **16f**).* This compound was prepared according to the general procedure (method A) from (R_P)-**18** (0.099 g, 0.5 mmol) and di-1-naphthylphosphine oxide (**11f**) (0.151 g, 0.5 mmol) yielding 14% of title compound containing 18% of (R_P,3S)-**17f**.

*(S_P,3R,4R)-3-(tert-Butylmethylphosphinoyl)-4-(di(1-naphthyl)-phosphinoyl)cyclohexene ((S_P,3R,4R)- **16f**).* This compound was prepared according to the general procedure (method A) from (R_P)-**18** (0.099 g, 0.5 mmol) and di-1-naphthylphosphine oxide (**11f**) (0.151 g, 0.5 mmol) yielding 3% of title compound containing 11% of (R_P,3R)-**17f**.

*(R_P,3S)-2-(tert-Butylmethylphosphinoyl)-3-(diphenylphosphinoyl)cyclohexene ((R_P,3S)-**17a**).* This compound was prepared according to the general procedure (method A) from (S_P)-**15** (0.200 g, 1.0 mmol) and diphenylphosphine oxide (**11a**) (0.204 g, 1.0 mmol) yielding 0.093 g (23%) of title compound: $[\alpha]_D$ = +17.0 (*c* 1.00, MeOH).

*(R_P,3R)-2-(tert-Butylmethylphosphinoyl)-3-(diphenylphosphinoyl)cyclohexene ((R_P,3S)-**17a**).* This compound was prepared according to the general procedure (method A) from (S_P)-**15** (0.200 g, 1.0 mmol) and diphenylphosphine oxide (**15a**) (0.204 g, 1.0 mmol) yielding 0.028 g (7%) of title compound: $[\alpha]_D$ = −26.8 (*c* 0.52, MeOH).

*(R_P,3S)-2-(tert-Butylmethylphosphinoyl)-3-(di(p-anisyl)-phosphinoyl)cyclohexene ((R_P,3S)-**17b**)* . This compound was prepared according to the general procedure (method A) from (S_P)-**15** (0.580 g, 2.9 mmol) and bis-*p*-anisylphosphine oxide (**11b**) (0.768 g, 2.9 mmol) yielding 25% of title compound containing 52% of **16b** both diastereoisomers

*(R_P,3R)-2-(tert-Butylmethylphosphinoyl)-3-(di(p-anisyl)-phosphinoyl)cyclohexene ((R_P,3R)-**17b**)* . This compound was prepared according to the general procedure (method A) from (S_P)-**15** (0.580 g, 2.9 mmol) and bis-*p*-anisylphosphine oxide (**11b**) (0.768 g, 2.9 mmol) yielding 0.052 g (4%) of title compound: $[\alpha]_D$ = −21.6 (*c* 0.51, MeOH).

*(R_P,3S)-2-(tert-Butylmethylphosphinoyl)-3-(di(1-naphthyl)-phosphinoyl)cyclohexene ((R_P,3S)-**17f**)* . This compound was prepared according to the general procedure (method A) from (R_P)-**18** (0.099 g, 0.5 mmol) and di-2-naphthylphosphine oxide (**11f**) (0.151 g, 0.5 mmol) yielding 18% of title compound containing 14% of (S_P,3S,4S)-**16f**.

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*(R_P,3R)-2-(tert-Butylmethylphosphinoyl)-3-(di(1-naphthyl)-phosphinoyl)cyclohexene ((R_P,3R)-**17f**)* . This compound was prepared according to the general procedure (method A) from (R_P)-**18** (0.099 g, 0.5 mmol) and di-2-naphthylphosphine oxide (**11f**) (0.151 g, 0.5 mmol) yielding 11% of title compound containing 3% of (S_P,3R,4R)-**16f**.

*(S_P,1R,2R)-1-(tert-Butylmethylphosphinoyl)-2-(diphenylphosphinoyl)-cyclohexane ((S_P,1R,2R)-**20a**)*. This compound was prepared according to the general procedure (method A) from (R_P)-**19** (0.053 g, 0.26 mmol), diphenylphosphine (0.048 g, 0.26 mmol) and *n*-butyllithium yielding 0.075 g (71%) of title compound: $[\alpha]_D$ = +16.6 (*c* 1.00, MeOH).

■ ASSOCIATED CONTENT

Supporting Information

Spectra of compounds **16a−c,f,g**, **17a−d,f,g**, **18**, **19**, and **20a,b,g,h**, HPLC of compounds **14** and **18**, and ORTEP of (S_P,1R,2R)-**20a** are presented. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b02337.

Spectra of compounds **16a−c,f,g**, **17a−d,f,g**, **18**, **19**, and **20a,b,g,h**, HPLC of compounds **14** and **18**, and ORTEP of (S_P,1R,2R)-**20a** (PDF)

Crystallographic data for compound (S_P,1R,2R)-**20a** (CIF)

Final atomic parameters have been deposited with the Cambridge Crystallographic Data Centre (no. CCDC 1446855).

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Notes

The authors declare no competing financial interest.

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