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P-chiral 1,7-diphosphanorbornenes: from asymmetric phospha-Diels–Alder reactions towards applications in asymmetric catalysis

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A straightforward synthesis of *P*-chiral polycyclic phosphines by an asymmetric Diels–Alder reaction of 1-alkyl-1,2-diphospholes and (5*R*)-(L-menthyloxy)-2(5*H*)-furanone (MOxF) is presented. The [4+2] cycloaddition reaction of 1,2-diphospholes **1-3** with MOxF (**4**) proceeded with high diastereoselectivity (*de* up to 90%) resulting in the corresponding enantiopure *anti-endo*-1,7-diphosphanorbornenes **5a-7a**. The absolute configuration of **5-7** was proved by a variety of 1D/2D NMR correlation methods. The use of the *anti-endo*-1,7-diphosphanorbornene **5a** in the Pd-catalyzed asymmetric allylic alkylation of cinnamyl acetate **8** with cyclic *β*-ketoesters **9a,b** provided up to 52% *ee*.

1. Introduction

The interest of *P*-chiral compounds concerns mainly agrochemistry, biology, drugs and ligands for asymmetric catalysis.[1] Surprisingly, tremendous efforts in recent decades have furnished new synthetic pathways towards *P*-chiral phosphines and triggered a comeback of these ligands.[2] Many methods can be used to prepare enantiomerically pure organophosphorus compounds, including resolution via diastereoisomers, chemical kinetic resolution, enzymatic resolution, chromatographic resolution and asymmetric catalysis.[2] In contrast to classical asymmetric carbon chemistry, in which a *C*-atom with trigonal-planar coordination is generally the prochiral species, all of these methods start from a *P*-atom in a trigonal–pyramidal or tetrahedral environment. In the last few years, the principle of diastereotopic face differentiation by employing a P=C double bond as prochiral motif, has been extended to organophosphorus compounds, [3] but this approach has attracted only little attention in the synthesis of *P*-chiral phosphines. Highly stereoselective hetero-Diels–Alder reactions of 1*H*- and transient 2*H*-phospholes with a chiral dienophile,[4] a chiral Al complex of 2-phosphindolizine[5] or a Pd complexes of 1-phenyl-3,4-dimethyl-1-monophosphole[6] proceeded with high diastereoselectivity and resulted in the corresponding enantiopure *P*-chiral polycyclic phosphines. An unprecedented phospha-aza-Diels–Alder reaction between an activated electron-poor imine and 2*H*-phospholes yielded 1-phospha-2-azanorbornenes in a highly chemoselective and moderately diastereoselective reaction.[7] Related 1-phosphanorbornadienes[8] have shown excellent results in asymmetric transition metal catalysis (*ee* values are 90-99%). The use of such rigid polycyclic phosphines[9] provides fixed *P*-chirality by a non-racemizable chiral phosphorus center, whose geometry precludes any loss of enantiomeric purity during catalysis or the associated recycling processes.[10]

At the same time, compared to the asymmetric carbo-, oxa- and aza-Diels-Alder reactions,[11] the phospha-Diels-Alder version still received much less attention,[12] as a major problem is the low stability of a P=C bond compared to a C=C bond.[13] Recently, we have contributed to this hardly explored field by applying a diastereoselective [4+2] cycloaddition reaction to 3,4,5-triaryl-1-(+)-neomenthyl-1,2-diphospholes as chiral diene with maleic acid derivatives as non-chiral dienophile (Scheme 1a).[14] In this way, the planarity and high reactivity of 1,2-diphospholes[15] allow to control the stereoselectivity in cycloaddition reactions using the principle of diastereotopic face differentiation by employing a P=C double bond as prochiral motif.[4] Herein, we present our detailed investigations on the diastereoselective Diels–Alder reaction of 1-alkyl-1,2-diphospholes as non-chiral diene and (5*R*)-(L-menthyloxy)-2(5*H*)-furanone (MOxF)[16] as chiral dienophile (Scheme 1b) and further applications of the obtained 1,7-diphosphanorbornenes as stereoinducers in the Pd-catalyzed asymmetric allylic alkylation of cinnamyl acetate with 2-oxocyclohexane-1-carboxylate and ethyl 2-oxocyclopentane-1-carboxylate. It should be noted that the Pd-catalyzed enantioselective synthesis of a quaternary carbon center is a complex problem, but provides access to practically useful building blocks.[17]

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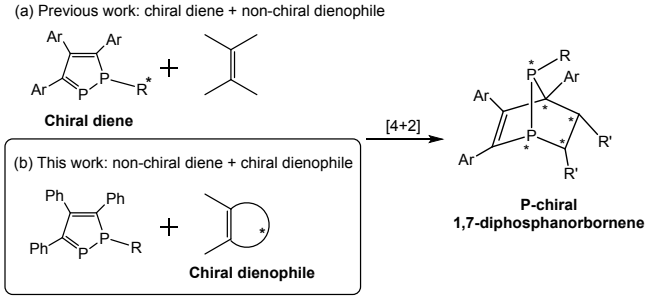
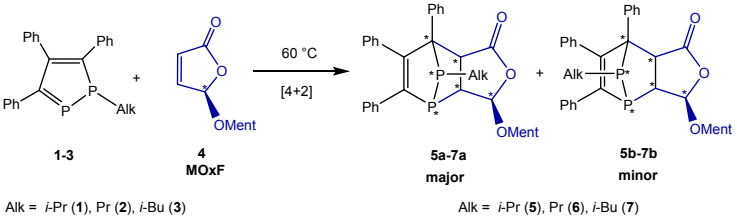


Scheme 1 (a) Cycloaddition of chiral 1-(+)-neomenthyl-1,2-diphospholes with non-chiral dienophiles; [14] (b) Cycloaddition of non-chiral 1-alkyl-1,2-diphospholes with chiral dienophiles.

2. Results and discussion

2.1. Synthesis of *P*-chiral 1,7-diphosphanorbornenes by an asymmetric phospha-Diels-alder reaction

Due to its cyclic structure and fixed chiral center, which is close to the C=C bond, (5*R*)-(L-menthyloxy)-2(5*H*)-furanone (MOxF)[16] is highly suitable for Diels–Alder reaction and has shown excellent selectivities in stereoselective reactions.[18] On the other hand, 1-alkyl-1,2-diphospholes combine the thermal stability of 1*H*-phospholes and high reactivity in cycloaddition reactions of 2*H*-phospholes.[14] Employing 3,4,5-triphenyl-1-alkyl-1,2-diphospholes (**1-3**) in asymmetric Diels–Alder reactions with MOxF (**4**) allows the generation of five new stereogenic centers in one step (Scheme 2). The reaction proceeds at 60 °C to give the [4+2] cycloaddition products, C_1-symmetric 1,7-diphosphanorbornenes **5a-7a**, with high diastereoselectivity up to 90% *de* (Table 1). The $^{31}P\{^1H\}$ NMR spectra of the reaction mixtures showed only four doublets – two doublets for each diastereomer. Higher temperatures (80–100 °C) gave lower *de* (80-83%) and lower yields for the major diastereomers **5a-7a**. However, lower temperatures required prolonged reaction times (4 days), and in these cases decomposition of 1-alkyl-1,2-diphospholes **1-3** took place slowly even at room temperature. In the optimized reaction conditions (60 °C, 20-22 h, toluene) the obtained diastereoselectivity was optimal. The stereoselectivity for the 1-isopropyl-1,2-diphosphole cycloadduct **5a** is better. On cooling the reaction mixture to -40 °C, the major diastereomers **5a-7a** crystallized with 65-70% yields, whereas the minor diastereomer **5b-7b** remained in solution. The $^{31}P\{^1H\}$ NMR spectra of **5a-7a** show two doublets between +91 and +72 as well as –39 and –35 ppm with $^1J_{PP}$ 198-204 Hz.



Scheme 2 Asymmetric phospha-Diels–Alder reaction of 1-alkyl-1,2-diphospholes **1-3** and MOxF **4**.

Table 1 Conditions and stereoselectivities for compounds **5a-7a** and **5b–7b**.

Entry	Alkyl	Conditions	anti : syn	*de*, %
1	*i*-Pr (**5a** and **5b**)	toluene, 25 °C, 4 d	20:1	90
2		toluene, 60 °C, 20 h	15:1	88
3		toluene, 80 °C, 10 h	11:1	83
4	Pr (**6a** and **6b**)	toluene, 25 °C, 4 d	12:1	85
5		toluene, 60 °C, 20 h	11:1	83
6	*i*-Bu (**7a** and **7b**)	toluene, 60 °C, 20 h	13:1	86
7		toluene, 100 °C, 8 h	9:1	80

[a] determined by ^1H NMR spectroscopy

3D structure determination of these products in solution is not trivial task therefore varieties of NMR correlation methods were used to resolve the problem (Figure 1). While for the major isomer **5a** the full structure (and absolute configuration as well) can be safely established, for the minor products **5b, c** only the diastereomeric structure of the tricycle can be derived with confidence.

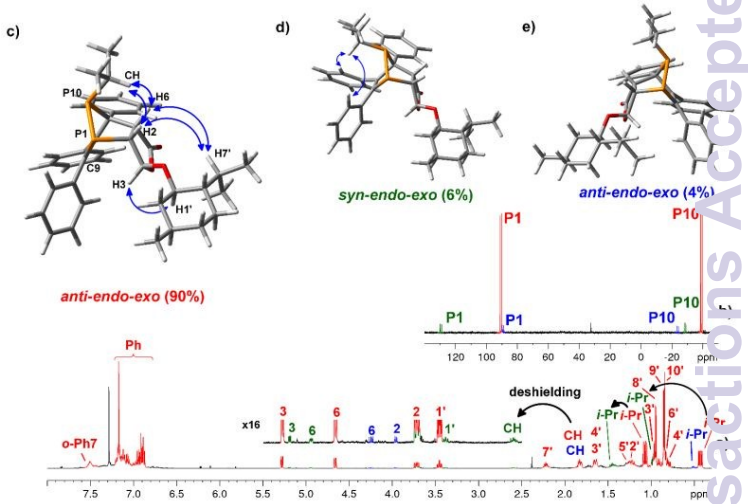


Fig. 1 (a) ^1H and (b) $^{31}P\{^1H\}$ NMR spectra of **5a** (c, red), **5b** (d, green) and **5c** (e, blue) with key NOE's (blue arrows) in $CDCl_3$ at T=303 K.

Firstly, from ^1H-^{31}P HMBC connectivities (SI) one can unambiguously correlate corresponding signals in ^{31}P and ^1H NMR spectra, at least for the tricyclic protons for all three isomers (Figure 1). Secondly, for the major product **5a**, ^1H-^1H COSY/TOCSY and ^1H-^{13}C HSQC/HMBC connectivities allow to assign all nuclei signals in ^1H and ^{13}C NMR spectra (SI). Thirdly, there are strong NOEs between *i*-Pr-P10 and H2/H6 protons, no NOEs between *i*-Pr-P10 and H3, and only small NOEs between H3 and H2, which unambiguously proves that the configuration of the tricyclic part is the *anti-endo-exo* (Figure 1). Moreover, small values of $^3J_{HH}$ between the protons H2 and H3 (ca. 2.4 Hz) are also attributed to their mutual *anti* orientation: calculations of $^3J_{HH}$ for **5*** (simplified model of **5** with *i*-Pr instead of menthyl) predict 7.6 and 2.5 Hz for the *endo* and *exo* isomer, respectively. This conclusion is also strongly supported by the calculated ^{31}P chemical shifts; the calculated chemical shifts

only agree well for the *anti-endo-exo* isomer with experimental data (Table 2). There is a strong NOE between H3 and H1' that suggests a *syn* orientation of these protons. Finally, there are NOEs between H2/H7' and H6/H7' that imply close proximity of these protons. Then, with the known absolute stereochemistry of MOxF, the configuration of the whole molecule is straightforward (*R* (P1), *R* (P10), *R* (C3), *R* (C1')).

The second isomer **5b** (~6%) has a noticeable low-field shift of P10. Based on calculated ^{31}P NMR data, this is a *syn* isomer at P10 (Table 2). This hypothesis is also strongly supported by experimental data. Namely, there are NOEs between *i*-Pr-P10 and the *ortho* protons H8/H9 of the phenyl ring indicating that the configuration at P10 is *syn*. Moreover, the low field shift of the *i*-Pr-P10 protons (if compared with the corresponding nuclei in the major isomer) is most probably due to in-plane deshielding effects of the phenyl rings in position 8 and 9 in this isomer. Calculations of the ^{1}H chemical shifts for these protons agree quite well with the experiment (Table 2).

The third isomer **5c** is formed in the lowest quantity (~4%) and is the most difficult to assign. However, based on the similarity of the ^{1}H and ^{31}P NMR data to the corresponding data for the major isomer (Table 2), it can be assumed that its tricyclic part has the same isomeric structure (*anti-endo-exo*) but with a reversed configuration (*S* (P1), *S* (P10), *S* (C3), *R* (C1')). This could be the product from MOxF with another stereochemistry ((5*S*)-(L-menthyloxy)-2(5*H*)-furanone) that, according to NMR data, is presented in small amounts (~4%) in the main product (SI).

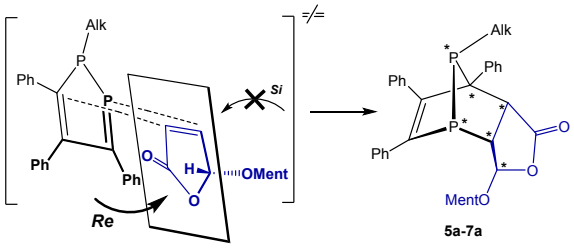
For **6a, b** and **7a, b, c** similar considerations lead to the same conclusions.

Table 2 Selected experimental and calculated ^{31}P and ^{1}H NMR chemical shifts for **5a**, **5b** and **5c**.

Experiment					
isomer		Amount (%) [a]		δ_{P10}, δ_{P1} ppm	δ_H *i*-Pr at P10 CH, Me, Me (ppm)
5a		90		90.6, -39.0	1.83, 1.07, 0.43
5b		5.8		129.5, -28.5	2.6, 1.42, 0.97
5c		4.2		89.4, -23.8	1.9, 1.08, 0.49
Calculation					
er	Configuration at C3	Energy, hartree	Relative energy, kcal/mol	δ_{P10}, δ_{P1}, ppm	δ_H *i*-Pr at P10 CH, Me, Me
anti-endo-exo	**R**	**-2380.7361219**	**0**	**88.5, -36.3**	**2.1, 0.9, 0.3**
syn-endo-exo	**R**	**-2380.7304603**	**3.6**	**128.7, -26.1**	**3.1, 1.2, 0.8**
anti-endo-exo	S	-2380.7357242	0.3	89.1, -35.0	
syn-endo-exo	S	-2380.7302608	3.7	128.3, -24.1	

[a] from ^{31}P{^{1}H} NMR spectra;

The observed selectivities can be explained by the transition state showing one attractive and three repulsive interactions (Scheme 3). Firstly, the attractive *endo* orientation of the transition state in [4+2] cycloaddition reactions is well known due to secondary orbital interactions of the HOMO (diene) and LUMO (dienophile).[19] Secondly, the sterically shielding L-menthyloxy group (OMent) of MOxF protects one side of the molecule from being attacked by 1-alkyl-1,2-diphospholes **1-3**, and a *Re*-face addition of the dienophile is expected for the cycloaddition reaction.[18] The above-mentioned interactions cause very good diastereoselectivity in a single concerted step and yield mainly one polycyclic rigid structure out of eight possible stereoisomers.



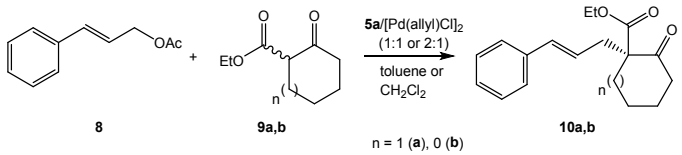
Scheme 3 Transition state of 1-alkyl-1,2-diphospholes and MOxF interaction.

From another point of view, the observed stereoselectivity of the reaction may also be due to the relative thermodynamic stability of possible isomers. For example, according to calculations (PBE1PBE/6-31+G(d)) for a **5*** (simplified model of **5** with *i*-Pr instead of menthyl), the *anti-endo-exo* form benefits in terms of energy compared to other isomers (2.2-12.8 kcal/mol, Table S1, SI). Moreover, considering that in real structures the *anti-endo-endo* isomers and forms with the L-menthyloxy group (OMent) connected to C5 are sterically disfavored, the next isomer with a low energy is the *syn-endo-exo* isomer, which is indeed also detected in the experiment.

2.2. Pd-catalyzed asymmetric allylic alkylation

Compounds **5a-7a** have been tested as ligands in the Pd-catalyzed asymmetric allylic alkylation of cinnamyl acetate (**8**). Ethyl 2-oxocyclohexane-1-carboxylate (**9a**) and ethyl 2-oxocyclopentane-1-carboxylate (**9b**) were chosen as nucleophiles (Scheme 4). In these challenging processes, a quaternary *C** stereocenter is generated on a carbon atom of the nucleophile, and achieving high enantioselectivity is not an easy task.[17h-k] In addition, there are only two examples for the synthesis of an enantioenriched **10b**.[17j,k]

Unfortunately, the application of ligands **6a** and **7a** in these reactions provided a very low conversion of **8**. Minor diastereomers **5b, c - 7b, c** were not tested in catalytic reactions, since they were not isolated individually. The obtained data using **5a** are summarized in Table 3.



Scheme 4 Pd-catalyzed asymmetric allylic alkylation of **8** with **9a, b**.

The efficiency of the catalytic system largely depends on the L/Pd molar ratio. The conversion of **8** at with an L/Pd ratio of 1:1 was approximately two times (in experiments with **9a**) and one and a half times (in experiments with **9b**) higher, than with a ratio of 2:1, regardless of the type of solvent. The highest enantioselectivity for both reactions was also obtained at an L/Pd ratio of 1:1 (52% and 42% *ee* for **10a** and **10b**, respectively; Table 3, entries 3 and 7). The choice of solvent also affects the reaction. The conversion of **8** and enantiomeric excesses of **10a, b** in experiments carried out in CH_2Cl_2 were higher compared with the results obtained in toluene. It should be noted that the effect of the L/Pd molar ratio on the asymmetric induction in toluene was the most significant (Table 3, entries 1/2 and 5/6).

Table 3 Pd-catalyzed allylation of **8** with **9a,b** using **5a**.[a]

Entry	Nucleophile	L/Pd	Solvent	Conversion (%)	*ee* (%)[d]
1[b]	**9a**	1	toluene	30	42 (*S*)
2[b]	**9a**	2	toluene	14	6 (*S*)
3[b]	**9a**	**1**	**CH_2Cl_2**	**51**	**52 (*S*)**
4[b]	**9a**	2	CH_2Cl_2	26	30 (*S*)
5[c]	**9b**	1	toluene	19	44 (*S*)
6[c]	**9b**	2	toluene	12	6 (*S*)
7[c]	**9b**	**1**	**CH_2Cl_2**	**26**	**47 (*S*)**
8[c]	**9b**	2	CH_2Cl_2	17	39 (*S*)

[a] Reactions were carried out with 2 mol% of $[Pd(allyl)Cl]_2$ at 20 °C for 48 h (BSA, $Zn(OAc)_2$).

[b] The conversion of **8** and enantiomeric excess of **10a** were determined by HPLC (Kromasil 5-CelluCoat, C_6H_{14}/*i*-PrOH = 95/5, 0.4 mL/min, 254 nm, t(*R*) = 14.3 min, t(*S*) = 16.4 min).

[c] The conversion of **8** and enantiomeric excess of **10b** were determined by HPLC (Chiralcel OD-H, C_6H_{14}/*i*-PrOH = 99/1, 0.6 mL/min, 254 nm, t(*R*) = 24.0 min, t(*S*) = 27.0 min).

[d] The absolute configuration of **10a** and **10b** was assigned by comparison of the HPLC retention times reported in the literature.[17b,c]

3. Experimental part

3.1. NMR Spectroscopy. All NMR experiments were performed with a Bruker AVANCE-500 spectrometer equipped with a 5 mm diameter gradient inverse broad band probehead and a pulsed gradient unit capable of producing magnetic field pulse gradients in the *z* direction of 53.5 G·cm^{-1}. Frequencies are 500.13 MHz in ^{1}H NMR, 202.5 MHz in ^{31}P NMR and 125.8 MHz in ^{13}C NMR experiments. For ^{1}H-^{31}P long range correlations, HMBC[20,21] experiments were optimized for J = 10 Hz. NOE experiments were performed with 1D DPFGNOE[22] techniques. Chemical shifts are reported in the δ (ppm) scale relative to the ^{1}H (7.27 ppm, trace amounts of $CHCl_3$) and ^{13}C (77.0 ppm) signals of in $CDCl_3$. ^{31}P chemical shifts were referred to 85% H_3PO_4 (0.00 ppm).

3.2. The quantum chemical calculations were performed with the Gaussian 03 software package.[23] Full geometry optimizations have been carried out within the framework of DFT (PBE1PBE) method using 6-31+G(d) basis sets. Chemical shifts were calculated at the PBE1PBE/6-311G(2d,2p) level of theory. ^{31}P chemical shifts were referred to H_3PO_4, and a linear scaling procedure was applied.[24] ^{1}H-^{1}H coupling constants were computed according to Bally and Rablen's recommendations.[25] First, the geometry was optimized at the B3LYP/6-31G(d) level. Then, a NMR single-point calculation of the Fermi contact J values was run at the B3LYP/6-31G(d,p) level. These values were then scaled by a factor of 0.9117.

3.3. Syntesis. All reactions and manipulations were carried out under dry pure N_2 in standard Schlenk devices. All solvents were distilled from sodium/benzophenone or P_2O_5 and stored under nitrogen before use. Infrared (IR) spectra were recorded on a Bruker Vector-22 spectrometer. The elemental analyses were carried out at the microanalysis laboratory of the Arbuzov Institute of Organic and Physical Chemistry, Russian Academy of Sciences

Starting materials: 1-alkyl-3,4,5-triphenyl-1,2-diphosphacyclopenta-2,4-dienes (**1-3**),[26] (5*R*)-(L-menthyloxy)-2(5*H*)-furanone (**4**) (MOxF),[16] $[Pd(allyl)Cl]_2$[27] were obtained according to literature procedures. *N*,*O*-bis(trimethylsilyl)acetamide (BSA), cinnamyl acetate (**8**), ethyl 2-oxocyclohexane-1-carboxylate (**9a**), and ethyl 2-oxocyclopentane-1-carboxylate (**9b**) were purchased from Aldrich or Acros and used without additional purification.

Synthesis of 10-isopropyl-7,8,9-triphenyl-4-oxa-1,10-diphosphatricyclo[5.2.1.0^{2,6}]-deca-8-ene-3-(L-menthyloxy)-5-one (5a). 0.29 g (1.21 mmol) of (5*R*)-(L-menthyloxy)-2(5*H*)-furanone (**4**) were added to solution of 0.45 g (1.21 mmol) 3,4,5-triphenyl-1-isopropyl-1,2-diphosphacyclopenta-2,4-diene (**1**) in 10 ml toluene and stirred for 20 hours at 60 °C. The solution was filtered and the solvent was evaporated at reduced pressure to leave 0.70 g (sum 95%) of a mixture of diastereomers (15:1, *de* = 88%) **5a** (major), **5b** and **5c** (minor). The major diastereoisomer **5a** was isolated by slow precipitation from 3 ml *n*-hexane at -40 °C. The precipitate was isolated and dried to give **5a** as a pale yellow powder (0.48 g, 65%) with m.p. 136 °C.

5a (90%). ^{1}H NMR ($CDCl_3$, δ, ppm, J, Hz): 7.56-7.46 (br, 2H, C7-*o*-Ph), 7.22-6.80 (m, 13H, C7-Ph, C8-Ph, C9-Ph), 5.28 (dd, 1H, $^3J_{HH}$ = 2.4, $^3J_{PH}$ = 8.7, C3-H), 4.66 (dd, 1H, $^3J_{HH}$ = 9.9, $^3J_{PH}$ = 2.4, C6-H), 3.72 (ddd, 1H, $^3J_{HH}$ = 2.4, $^3J_{HH}$ = 9.9, $^2J_{PH}$ = 16.0, C2-H), 3.45 (td, 1H,$^3J_{HH}$ = 10.7, $^3J_{HH}$ = 4.2, C1'-H), 2.22 (ttd, 1H, $^3J_{HH}$ = 7.0, $^3J_{HH}$ = 7.0, $^3J_{HH}$ = 2.6, C7'-H),

1.88-1.78 (m, 2H, C11-H, C6'-H), 1.68-1.61 (m, 2H, C3'-H, C4'-H), 1.32-1.15 (m, 2H, C5'-H, C2'-H), 1.06 (dd, 3H, $^3J_{HH}$ = 7.0, $^3J_{PH}$ = 13.3, C12-H), 1.00-0.93 (m, 1H, C3'-H), 0.95 (d, 3H, $^3J_{HH}$ = 7.0, C8'-H), 0.85 (d, 3H, $^3J_{HH}$ = 7.0, C9'-H), 0.84 (d, 3H, $^3J_{HH}$ = 7.0, C10'-H), 0.88-0.76 (m, 2H, C4'-H, C6'-H), 0.43 (ddd, 3H, $^3J_{HH}$ = 8.3, $^3J_{PH}$ = 14.4, $^4J_{PH}$ = 0.8, C13-H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ, ppm, J, Hz): 176.59 (s, C5), 159.48 (dd, $^2J_{CP}$ = 16.7, $^2J_{CP}$ = 4.6, C8), 139.90 (d, $^2J_{CP}$ = 20.7, *ipso*-$C9_{Ph}$), 139.32 (dd, $^1J_{CP}$ = 25.0, $^2J_{CP}$ = 18.5, C9), 138.28 (d, $^2J_{CP}$ = 5.3, *ipso*-$C7_{Ph}$), 136.17 (dd, $^3J_{CP}$ = 2.2, $^3J_{CP}$ = 1.4, *ipso*-$C8_{Ph}$), 130.73 (s, *o*-$C8_{Ph}$), 130.33 (br, *o*-$C7_{Ph}$), 130.00 (dd, $^3J_{CP}$ = 8.4, $^4J_{CP}$ = 2.4, *o*-$C9_{Ph}$), 128.14 (s, *m*-$C9_{Ph}$), 127.44 (s, *m*-$C8_{Ph}$), 127.33 (s, *m*-$C7_{Ph}$), 127.00 (s, *p*-$C8_{Ph}$), 126.94 (d, $^5J_{CP}$ = 1.9, *p*-$C9_{Ph}$), 126.23 (d, $^5J_{CP}$ = 2.4, *p*-$C7_{Ph}$), 100.38 (d, $^3J_{CP}$ = 14.5, C3), 77.58 (s, C1'), 76.58 (dd, $^1J_{CP}$ = 28.7, $^2J_{CP}$ = 4.6, C7), 50.69 (d, $^1J_{CP}$ = 31.9, C2), 47.76 (dd, $^2J_{CP}$ = 2.6, $^2J_{CP}$ = 2.6, C6), 47.76 (s, C2'), 39.80 (s, C6'), 34.24 (s, C4'), 31.29 (s, C5'), 26.65 (d, $^1J_{CP}$ = 32.9, C11), 25.41 (s, C7'), 23.02 (s, C3'), 22.06 (s, C10'), 20.98 (s, C8'), 20.14 (dd, $^2J_{CP}$ = 13.5, $^3J_{CP}$ = 4.6, C12), 19.63 (dd, $^2J_{CP}$ = 18.9, $^3J_{CP}$ = 3.8, C13), 15.62 (s, C9'). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ, ppm, J, Hz): 90.7 (d, $^1J_{CP}$ = 203.3, P10), -39.1 (d, $^1J_{CP}$ = 203.3, P1). IR (KBr, cm^{-1}): 457 (w), 496 (w), 578 (w), 645 (w), 696 (s), 739 (m), 756 (m), 772 (m), 802 (s), 873 (w), 919 (w), 954 (m), 1026 (br.s, C-O-C), 1103 (br.s, C-O-C), 1154 (m), 1262 (s), 1347 (w), 1443 (m), 1492 (w), 1597 (w), 1765 (s, CO), 2863 (m), 2921 (m), 2956 (m), 3024 (w), 3057 (w). $[\alpha]^{25}_D$ = -104° (c 0.5, THF). Found: C 74.50, H 7.33, P 10.28. Calculated for $C_{38}H_{44}O_3P_2$: C 74.74, H 7.26, O 7.86, P 10.14.

5b (6%). ^1H NMR ($CDCl_3$, δ, ppm, J, Hz): 5.19 (dd, 1H, $^3J_{HH}$ = 2.4, $^3J_{PH}$ = 8.7, C3-H), 4.95 (ddd, 1H, $^3J_{HH}$ = 9.9, $^3J_{PH}$ = 4.3, $^3J_{PH}$ = 2.4, C6-H), 3.75-3.65 (m, 1H, C2-H), 3.38 (td, 1H,$^3J_{HH}$ = 10.7, $^3J_{HH}$ = 4.2, C1'-H), 2.64-2.55 (m, 2H, C11-H), 1.44-1.39 (m, 3H, C12-H), 1.00-0.92 (m, 3H, C13-H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ, ppm, J, Hz): 101.7 (C3), 77.9 (C1'), 47.7 (C6), 43.9 (C2), 24.3 (C12), 22.4 (C11), 22.2 (C13) (from HSQC spectra). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ, ppm, J, Hz): 129.5 (d, $^1J_{CP}$ = 203.3, P10), -28.6 (d, $^1J_{CP}$ = 203.3, P1).

5c (4%). ^1H NMR ($CDCl_3$, δ, ppm, J, Hz): 4.25 (dd, 1H, $^3J_{HH}$ = 12.2, $^3J_{PH}$ = 9.3, C6-H), 3.96 (d, 1H, $^2J_{PH}$ = 9.2, C2-H), 1.95-1.85 (m, 2H, C11-H), 0.49 (ddd, 3H, $^3J_{HH}$ = 8.5, $^3J_{PH}$ = 11.2, $^4J_{PH}$ = 0.8, C13-H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ, ppm, J, Hz): 51.8 (C2), 48.7 (C6), 26.7 (C11), 19.6 (C13) (from HSQC spectra). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ, ppm, J, Hz): 89.3 (d, $^1J_{CP}$ = 203.3, P10), -23.8 (d, $^1J_{CP}$ = 203.3, P1).

Synthesis of 10-propyl-7,8,9-triphenyl-4-oxa-1,10-diphosphatricyclo[5.2.1.0^{2,6}]-deca-8-ene-3-(L-menthyloxy)-5-one (6a). 0.26 g (1.08 mmol) of (5*R*)-(L-menthyloxy)-2(5*H*)-furanone (**4**) were added to solution of 0.4 g (1.08 mmol) 3,4,5-triphenyl-1-propyl-1,2-diphosphacyclopenta-2,4-diene (**2**) in 10 ml toluene and stirred for 22 hours at 60 °C. The solution was filtered and the solvent was evaporated at reduced pressure to leave 0.63 g (sum 95%) of a mixture of diastereomers (11:1, *de* = 83%) **6a** (major) and **6b** (minor). The major diastereoisomer **6a** was isolated by slow precipitation from 3 ml *n*-hexane at -40 °C. The precipitate was isolated and dried to give **6a** as a pale yellow powder (0.46 g, 70%) with m.p. 137 °C.

6a (89%). ^1H NMR ($CDCl_3$, δ, ppm, J, Hz): 7.49 (d, 2H, $^4J_{PH}$ = 7.6, C7-*o*-Ph), 7.27-6.85 (m, 13H, C7-Ph, C8-Ph, C9-Ph), 5.31 (dd, 1H, $^3J_{HH}$ = 2.5, $^3J_{PH}$ = 8.7, C3-H), 4.59 (dd, 1H, $^3J_{HH}$ = 9.9, $^3J_{PH}$ = 2.3, C6-H), 3.76 (ddd, 1H, $^3J_{HH}$ = 2.4, $^3J_{HH}$ = 12.6, $^2J_{PH}$ = 15.0, C2-H), 3.47 (td, 1H,$^3J_{HH}$ = 10.9, $^3J_{HH}$ = 4.2, C1'-H), 2.24 (ttd, 1H, $^3J_{HH}$ = 7.0, $^3J_{HH}$ = 7.0, $^3J_{HH}$ = 2.6, C7'-H), 1.81 (br d, 1H, $^2J_{HH}$ = 11.6, C6'-H), 1.68-1.62 (m, 2H, C3'-H, C4'-H), 1.33-1.28 (m, 4H, C11-H, C12-H), 1.27-1.19 (m, 2H, C5'-H, C2'-H), 1.02-0.98 (m, 1H, C3'-H), 0.96 (d, 3H, $^3J_{HH}$ = 7.2, C8'-H), 0.86 (d, 3H, $^3J_{HH}$ = 6.9, C9'-H), 0.88-0.85 (m, 3H, C13-H), 0.85 (d, 3H, $^3J_{HH}$ = 6.4, C10'-H), 0.85-0.80 (m, 2H, C4'-H, C6'-H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ, ppm, J, Hz): 176.54 (s, C5), 158.92 (dd, $^2J_{CP}$ = 18.0, $^2J_{CP}$ = 4.5, C8), 140.42 (dd, $^1J_{CP}$ = 26.0, $^2J_{CP}$ = 19.3, C9), 139.93 (d, $^2J_{CP}$ = 20.2, *ipso*-$C9_{Ph}$), 137.68 (d, $^2J_{CP}$ = 5.7, *ipso*-$C7_{Ph}$), 136.18 (dd, $^3J_{CP}$ = 2.2, $^3J_{CP}$ = 1.4, *ipso*-$C8_{Ph}$), 130.67 (s, *o*-$C8_{Ph}$), 130.11 (d, $^2J_{CP}$ = 10.8, *o*-$C7_{Ph}$), 129.96 (dd, $^3J_{CP}$ = 8.4, $^4J_{CP}$ = 2.4, *o*-$C9_{Ph}$), 128.18 (s, *m*-$C9_{Ph}$), 127.46 (s, *m*-$C8_{Ph}$), 127.38 (s, *m*-$C7_{Ph}$), 127.03 (d, $^5J_{CP}$ = 1.9, *p*-$C8_{Ph}$), 126.96 (d, $^5J_{CP}$ = 2.4, *p*-$C9_{Ph}$), 126.27 (s, *p*-$C7_{Ph}$), 100.32 (d, $^3J_{CP}$ = 14.5, C3), 77.48 (s, C1'), 76.80 (dd, $^1J_{CP}$ = 26.2, $^2J_{CP}$ = 4.1, C7), 50.87 (d, $^1J_{CP}$ = 32.4, C2), 47.84 (dd, $^2J_{CP}$ = 3.6, $^2J_{CP}$ = 2.6, C6), 47.73 (s, C2'), 39.84 (s, C6'), 34.24 (s, C4'), 31.29 (s, C5'), 26.93 (d, $^1J_{CP}$ = 36.0, C11), 25.40 (s, C7'), 23.01 (s, C3'), 22.05 (s, C10'), 20.98 (s, C8'), 19.69 (dd, $^2J_{CP}$ = 16.8, $^3J_{CP}$ = 3.2, C12), 15.62 (s, C9'), 15.45 (dd, $^3J_{CP}$ = 10.5, $^4J_{CP}$ = 1.0, C13). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ, ppm, J, Hz): 73.7 (d, $^1J_{CP}$ = 198.3, P10), -37.2 (d, $^1J_{CP}$ = 203.3, P1). IR (KBr, cm^{-1}): 497 (w), 578 (w), 645 (w), 695 (s), 739 (m), 756 (m), 772 (m), 802 (s), 873 (w), 955 (m), 1027 (br.s, C-O-C), 1103 (br.s, C-O-C), 1152 (m), 1262 (s), 1348 (w), 1444 (m), 1491 (w), 1498 (m), 1595 (w), 1762 (s, CO), 2862 (m), 2921 (m), 2956 (m), 3021 (w). $[\alpha]^{25}_D$ = -102° (c 0.5, THF). Found: C 74.56, H 7.20, P 10.29. Calculated for $C_{38}H_{44}O_3P_2$: C 74.74, H 7.26, P 10.14.

6b (9%). ^1H NMR ($CDCl_3$, δ, ppm, J, Hz): 4.26 (dd, 1H, $^3J_{HH}$ = 11.7, $^3J_{PH}$ = 9.3, C6-H), 3.98 (d, 1H, $^2J_{PH}$ = 9.1, C2-H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ, ppm, J, Hz): 52.4 (C2), 48.4 (C6) (from HSQC spectra). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ, ppm, J, Hz): 71.8 (d, $^1J_{CP}$ = 200.7, P10), -21.9 (d, $^1J_{CP}$ = 200.7, P1).

Synthesis of 10-isobutyl-7,8,9-triphenyl-4-oxa-1,10-diphosphatricyclo[5.2.1.0^{2,6}]-deca-8-ene-3-(L-menthyloxy)-5-one (7a). 0.25 g (1.04 mmol) of (5*R*)-(L-menthyloxy)-2(5*H*)-furanone (**4**) were added to solution of 0.40 g (1.04 mmol) 3,4,5-triphenyl-1-isobutyl-1,2-diphosphacyclopenta-2,4-diene (**3**) in 10 ml toluene and stirred for 20 hours at 60 °C. The solution was filtered and the solvent was evaporated at reduced pressure to leave 0.62 g (sum 95%) of a mixture of diastereomers (13:1, *de* = 86%) **7a** (major), **7b** and **7c** (minor). The major diastereoisomer **7a** was isolated by slow precipitation from 3 ml *n*-hexane at -40 °C. The precipitate was isolated and dried to give **7a** as a pale yellow powder (0.44 g, 68%) with m.p. 140 °C.

7a (89%). ^1H NMR ($CDCl_3$, δ, ppm, J, Hz): 7.47 (d, 2H, $^4J_{PH}$ = 7.8, C7-*o*-Ph), 7.27-6.85 (m, 13H, C7-Ph, C8-Ph, C9-Ph), 5.29 (dd, 1H, $^3J_{HH}$ = 2.5, $^3J_{PH}$ = 8.6, C3-H), 4.54 (dd, 1H, $^3J_{HH}$ = 9.9, $^3J_{PH}$ = 2.3, C6-H), 3.74 (ddd, 1H, $^3J_{HH}$ = 2.4, $^3J_{HH}$ = 12.6, $^2J_{PH}$ = 15.0, C2-H), 3.45 (td, 1H,$^3J_{HH}$ = 10.9, $^3J_{HH}$ = 4.2, C1'-H), 2.23 (ttd, 1H, $^3J_{HH}$ = 7.0, $^3J_{HH}$ = 7.0, $^3J_{HH}$ = 2.6, C7'-H), 1.79 (br d, 1H, $^2J_{HH}$ = 11.6, C6'-H), 1.68-1.62 (m, 2H, C3'-H,

C4'-H), 1.61-1.55 (m, 1H, C11-H), 1.54-1.49 (m, 1H, C12-H), 1.19-1.12 (m, 1H, C12-H), 1.27-1.19 (m, 2H, C5'-H, C2'-H), 1.02-0.92 (m, 1H, C3'-H), 0.95 (d, 3H, $^3J_{HH}$ = 7.2, C8'-H), 0.88 (d, 3H, $^3J_{HH}$ = 6.4, C13-H), 0.85 (d, 3H, $^3J_{HH}$ = 6.9, C9'-H), 0.84 (d, 3H, $^3J_{HH}$ = 6.5, C10'-H), 0.85-0.77 (m, 2H, C4'-H, C6'-H), 0.79 (d, 3H, $^3J_{HH}$ = 6.4, C14-H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ, ppm, J, Hz): 176.54 (s, C5), 158.86 (dd, $^2J_{CP}$ = 18.0, $^2J_{CP}$ = 4.5, C8), 140.73 (dd, $^1J_{CP}$ = 26.0, $^2J_{CP}$ = 19.3, C9), 139.93 (d, $^2J_{CP}$ = 20.2, *ipso*-$C9_{Ph}$), 137.54 (d, $^2J_{CP}$ = 5.7, *ipso*-$C7_{Ph}$), 136.27 (dd, $^3J_{CP}$ = 2.2, $^3J_{CP}$ = 1.4, *ipso*-$C8_{Ph}$), 130.70 (s, *o*-$C8_{Ph}$), 130.16 (d, $^2J_{CP}$ = 10.8, *o*-$C7_{Ph}$), 129.98 (dd, $^3J_{CP}$ = 8.4, $^4J_{CP}$ = 2.4, *o*-$C9_{Ph}$), 128.19 (s, *m*-$C9_{Ph}$), 127.46 (s, *m*-$C8_{Ph}$), 127.38 (s, *m*-$C7_{Ph}$), 127.03 (s, *p*-$C8_{Ph}$), 126.96 (d, $^5J_{CP}$ = 1.9, *p*-$C9_{Ph}$), 126.29 (d, $^5J_{CP}$ = 2.4, *p*-$C7_{Ph}$), 100.32 (d, $^3J_{CP}$ = 14.5, C3), 77.52 (s, C1'), 76.80 (dd, $^1J_{CP}$ = 25.3, $^2J_{CP}$ = 4.0, C7), 50.91 (d, $^1J_{CP}$ = 32.4, C2), 47.92 (dd, $^2J_{CP}$ = 3.6, $^2J_{CP}$ = 2.6, C6), 47.94 (s, C2'), 39.84 (s, C6'), 34.24 (s, C4'), 34.14 (d, $^1J_{CP}$ = 37.3, C11), 31.31 (s, C5'), 26.90 (dd, $^1J_{CP}$ = 36.0, $^2J_{CP}$ = 2.6, C12), 25.39 (s, C7'), 23.87 (d, $^3J_{CP}$ = 9.0, C13), 23.69 (dd, $^3J_{CP}$ = 7.5, $^4J_{CP}$ = 2.1, C14), 23.01 (s, C3'), 22.07 (s, C10'), 21.00 (s, C8'), 15.62 (s, C9'). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ, ppm, J, Hz): 73.7 (d, $^1J_{CP}$ = 198.3, P10), -37.2 (d, $^1J_{CP}$ = 203.3, P1). IR (KBr, cm^{-1}): 457 (w), 577 (w), 644 (w), 694 (s), 739 (m), 772 (m), 805 (s), 873 (w), 953 (m), 1026 (br.s, C-O-C), 1105 (br.s, C-O-C), 1154 (m), 1261 (s), 1347 (w), 1442 (m), 1491 (w), 1492 (m), 1597 (w), 1764 (s, CO), 2863 (m), 2922 (m), 2956 (m), 3057 (w). $[\alpha]^{25}_D$ = -109° (c 0.5, THF). Found: C 74.76, H 7.59, P 10.09. Calculated for $C_{39}H_{46}O_3P_2$: C 74.98, H 7.42, P 9.92.

7b (2%). ^1H NMR ($CDCl_3$, δ, ppm, J, Hz): 5.23 (dd, 1H, $^3J_{HH}$ = 3.3, $^3J_{PH}$ = 8.5, C3-H), 4.95-4.90 (m, 1H, C6-H), 3.84-3.79 (m, 1H, C2-H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ, ppm, J, Hz): 101.2 (C3), 46.7 (C6), 44.9 (C2) (from HSQC spectra). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ, ppm, J, Hz): 110.7 (d, $^1J_{CP}$ = 192.4, P10), -24.7 (d, $^1J_{CP}$ = 192.4, P1).

7c (8%). ^1H NMR ($CDCl_3$, δ, ppm, J, Hz): 4.24 (dd, 1H, $^3J_{HH}$ = 11.7, $^3J_{PH}$ = 9.3, C6-H), 3.84 (d, 1H, $^2J_{PH}$ = 9.1, C2-H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ, ppm, J, Hz): 51.8 (C2), 48.0 (C6) (from HSQC spectra). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ, ppm, J, Hz): 69.6 (d, $^1J_{CP}$ = 200.7, P10), -20.4 (d, $^1J_{CP}$ = 200.7, P1).

3.4. General procedure for catalytic reactions. A solution of $[Pd(allyl)Cl]_2$ (0.0019 g, 0.005 mmol) and **5a** (0.01 mmol or 0.02 mmol) in an appropriate solvent (1.5 mL) was stirred for 40 min. Cinnamyl acetate (**8**) (0.04 mL, 0.25 mmol) was added and the solution stirred for 15 min. Ethyl 2-oxocyclohexane-1-carboxylate (**9a**) or ethyl 2-oxocyclopentane-1-carboxylate (**9b**) (0.375 mmol), BSA (0.25 mL, 1 mmol) and $Zn(OAc)_2$ (0.005 g) were added. The reaction mixture was stirred for 48 h, diluted with the appropriate solvent (2 mL) and filtered through a thin layer of SiO_2. The solvent was evaporated at reduced pressure (40 torr) and dried in vacuum (10 torr) affording a residue containing ethyl 1-cinnamyl-2-oxocyclohexanecarboxylate (**10a**) or ethyl 1-cinnamyl-2-oxocyclopentanecarboxylate (**10b**), respectively.[17b,c] In order to evaluate the *ee* and conversion, the obtained residue was dissolved in an appropriate eluent mixture (8 mL) and analyzed by HPLC.

4. Conclusions

The principle of stereotopic face differentiation can be successfully applied to 3,4,5-triphenyl-1–alkyl-1,2-diphospholes (**1-3**) which undergo a very efficient and highly stereoselective Diels–Alder reaction with (5*R*)-(L-menthyloxy)-2(5*H*)-furanone (**4**) giving *P*-chiral 1,7-diphosphanorbornenes **5a-7a** (80-90% *de*). The occurrence of mainly one out of eight possible stereoisomers can be explained by the transition states of the Diels-Alder reactions showing one attractive and other repulsive interactions. The stereochemistry including the absolute configuration of **5-7** was unequivocally proved by a variety of 1D/2D NMR correlation methods. The use of **5a** as ligand in the Pd-catalyzed asymmetric allylic alkylation of cinnamyl acetate (**8**) with cyclic ethyl 2-oxocyclohexane-1-carboxylate (**9a**) and ethyl 2-oxocyclopentane-1-carboxylate (**9b**) provided up to 52% and 47% *ee*, respectively. In conclusion, asymmetric [4+2] cycloaddition reaction of 1-alkyl-1,2-diphospholes can be used as a new synthetic tool for the selective and efficient synthesis of *P*-chiral polycyclic phosphines from readily available and cheap starting materials. Moreover, the introduced chiral auxiliary enables further functionalization, such as reductive cleavage or substitution reactions, which are of interest for the synthesis of water-soluble chiral phosphines and subsequent ligand design for asymmetric catalysis.

Conflicts of interest

There are no conflicts to declare.

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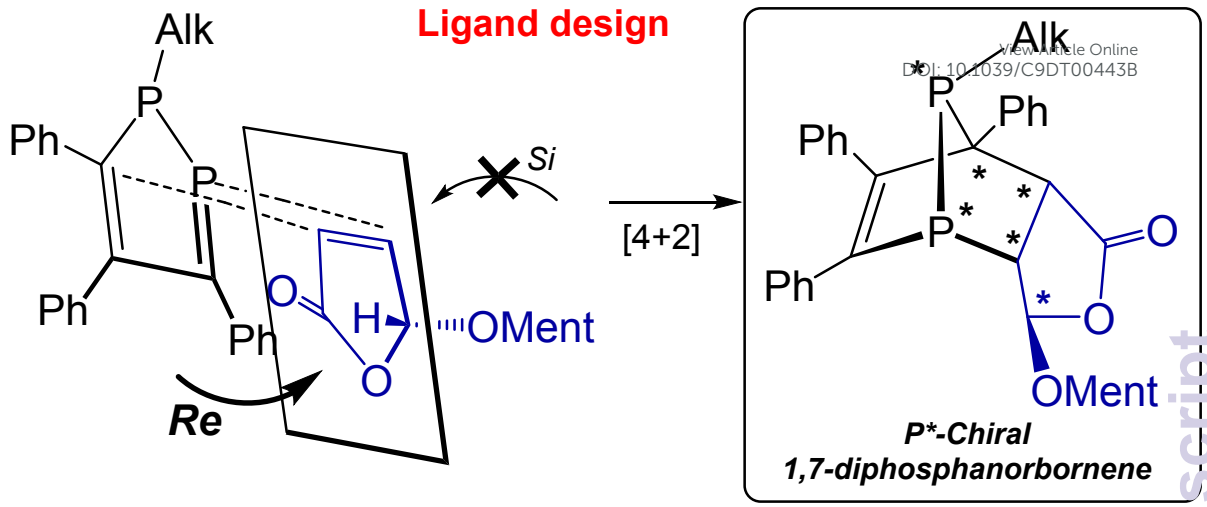
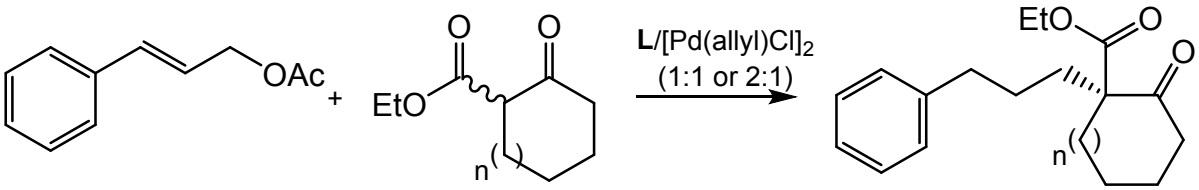


Asymmetric catalysis



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