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Dynamic Kinetic Resolution of Phosphinic Acid Derivatives via Nucleophilic Substitution at Phosphorus Center

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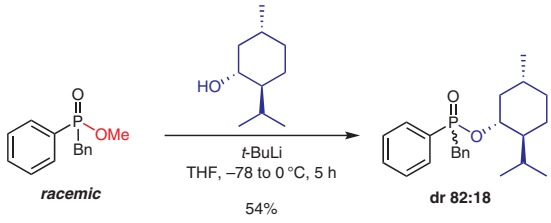

DKR-like process based on different reactivity of each enantiomer

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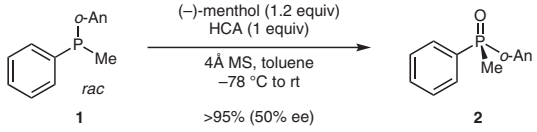
Abstract Reaction of racemic phosphinic acid derivatives with chiral alcohols proceeds with predominant formation of one diastereomer. The highest level of enrichment has been obtained for transesterfication of racemic methyl benzylphenylphosphinate (64% de). The outcome of the reaction depends on both the structure of chiral alcohol and the starting organophosphorus compound. The results strongly suggest that the nature of the observed phenomena is not a classical equilibration of intermediates found in dynamic kinetic resolution process but is a result of a different reactivity of both enantiomers of racemic substrate towards the same chiral nucleophile.

Key words phosphinic acid derivatives, transesterification, dynamic kinetic resolution, Berry pseudorotation, stereochemistry

In the last decades, chiral organophosphorus compounds have become one of the main research topics in organophosphorus chemistry due to their utility as ligands in asymmetric catalysis.[1] Among known ligands, the vast majority of them possess the chirality center at the carbon atom (DIOP, BINAP)[2] and not at the phosphorus (DIPAMP)[3] although the latter should give better performances in catalytic transformations. This is due to the fact that the chirality in P-stereogenic molecules is located in the closest proximity to the catalytic center, which is believed to have a beneficial effect on stereoselectivity of catalytic process.[4] Nowadays, however, *C*-chiral phosphines have dominated the asymmetric catalysis as the nonracemic *P*-stereogenic compounds still represent a challenging synthetic task. The most known synthetic routes leading to *P*-stereogenic organophosphorus compounds are those based on a *chiral auxiliary* approach, like ephedrine-based synthesis of *P*-stereogenic phosphines and their derivatives[5] or sparteine-mediated desymmetrization of prochiral phosphine derivatives.[6] Although efficient, the above methods lack generality so the development of a general methodology that allows the preparation of nonracemic *P*-stereogenic compounds for potential applications in the synthesis and catalysis is still an attractive research topic.

As a part of our ongoing interest in discovering new pathways for the synthesis of chiral phosphine ligands our attention has been focused on *kinetic resolution*/*dynamic kinetic resolution* (KR/DKR) strategies. The basis of the first strategy may rely, for example, on the different reaction rates of both enantiomers with the same chiral reagent or catalyst[7] whereas the latter strategy is based on preferential epimerization of one of the enantiomers under the reaction conditions prior to its transformation into the product.[8] The first report on kinetic resolution of organophosphorus compounds was made by Wittig and co-workers who described partial resolution of *p*-(biphenylyl)(1-naphthyl)phenylphosphine using paraformaldehyde and (+)-camphor-10-sulfonic acid.[9] Since then, some progress in this field has been made using enzymatic[10] or chemical transformations.[11] Recently, a very promising DKR of racemic *P*-stereogenic phosphines and their derivatives has been developed by Gilheany and co-workers (Scheme 1).[12]



Scheme 1 Dynamic kinetic resolution of **1** using Appel reaction

This method is based on the transformation of racemic phosphines or phosphine oxides into the corresponding enantioenriched *P*-stereogenic phosphine oxides under Appel conditions using hexachloroacetone (HCA) as a source of positive halogen and a chiral alcohol as a source of chirality. According to the mechanism suggested by the authors, the

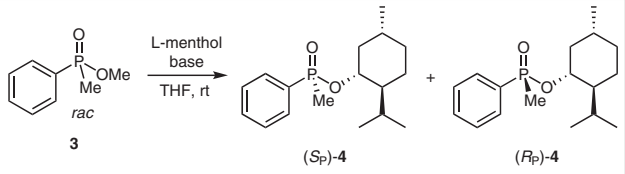
first step is a reaction between the free racemic phosphine with hexachloroacetone, which affords the corresponding chlorophosphonium salt. The latter undergoes a reaction with the chiral alcohol leading to two diastereomeric pentavalent organophosphorus intermediates. These intermediates undergo fast interconversion through Berry pseudorotation,[13] which results in the configurational instability of phosphorus center. Halide atom cleavage leads to the corresponding alkoxyphosphonium salts, which are configurationally stable and afford the desired enriched phosphine oxides upon a C–O bond cleavage by a chloride anion. The crucial point in the proposed transformation is the relative stability of the pentavalent intermediates and their transformation rates into alkoxyphosphonium salts and then phosphine oxides. The more they differ, the higher level of dynamic kinetic resolution is reached.

For DKR to occur, two conditions must be fulfilled. First, pentavalent intermediates must be relatively stable, as only in this case does Berry pseudorotation have a chance to take place. Second, the transformation of the pentavalent intermediates into the product should occur at different rates. For high DKR levels it is preferred that the more stable intermediate is formed in high excess and the rate of leaving group cleavage is at least the same for both isomers.

The formation of pentavalent organophosphorus intermediate, as suggested by Gilheany and co-workers, is the crucial element for the formation of enantiomerically enriched product as these compounds are known to undergo Berry pseudorotation.[13] In the case of chiral compounds, this process usually results in extended racemization of chiral substrate. But, at the same time, the same process can induce the formation of enriched product if: a) chiral reagent is used and b) the formed pentavalent intermediate is stable enough to undergo Berry pseudorotation under the reaction conditions prior to leaving group cleavage. Potentially, the simplest method for the formation of intermediate pentavalent organophosphorus compounds is the bimolecular nucleophilic substitution reaction at phosphorus. This process is well established for carbon compounds as S_N2 reaction, but organophosphorus compounds, especially P(V) compounds, undergo this transformation in a far more complex manner.[14] Despite its operational simplicity, bimolecular nucleophilic substitution might be a potentially useful pathway for the synthesis of nonracemic *P*-stereogenic compounds from racemic substrates.

The relative stability of the intermediates discussed above can be assured by the proper choice of the transformation, at least partially. It is assumed that transesterification of phosphinic acid esters might be a good candidate as both the nucleophile and leaving group are alkoxy anions with similar pKa values. Transesterification of phosphorus esters is one of the key processes in the chemistry of phosphorus acid derivatives, which can be performed by traditional[15] or modern[16] methods.

Based on the assumptions discussed above, a reaction of chiral menthoxy anion with racemic methyl methylphenylphosphinate (**3**) was performed as a model for a potential DKR process (Scheme 2).



(S_P)-**4** (R_P)-**4**

		conv.	dr
L-menthol (1.0 equiv)/NaH (1.0 equiv)	3 h	29%	80:20
	18 h	62%	48:52
L-menthol (1.0 equiv)/*n*-BuLi (1.1 equiv)	30 min	53%	75:25
	17 h	72%	73:27
L-menthol (1.5 equiv)/*n*-BuLi (1.7 equiv)	30 min	87%	73:27
	1 h	100%	73:27

Scheme 2 Initial experiments on DKR of racemic phosphinic ester **3**

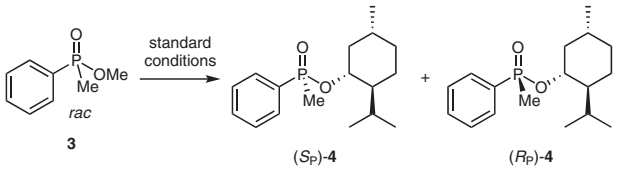
First, a reaction of racemic **3** with an equimolar amount of sodium L-menthoxide was monitored using ^{31}P NMR technique. After 3 hours, the conversion of the substrate was only 29% but the ratio of the diastereomers (S_P)-**4**/(R_P)-**4** reached 80:20. Surprisingly, after 18 hours, the amount of diastereomers was practically equal and the conversion reached 62%. Then, racemic **3** was subjected to the reaction with an equimolar amount of lithium L-menthoxide. The conversion of the substrate after 30 minutes was remarkably higher compared to a reaction with sodium L-menthoxide (53% vs 29%) and the diastereomeric ratio was similar in both cases. What is more interesting, the ratio of the diastereomers remained at the same level when the reaction was monitored after 17 hours, which was not the case for sodium L-menthoxide. When the reaction was carried in the presence of 1.5-fold excess of lithium L-menthoxide, the conversion of **3** into products reached 87% after only 30 minutes, and after 1 hour, there was no substrate left in the reaction mixture. Diastereomeric ratios of the products appeared to be the same as in previous reaction (73:27).

The reaction course for sodium L-menthoxide is quite unusual as in the first period the predominant formation of S_P diastereomer was observed whereas in the second stage the formation of the opposite diastereomer was dominating. The overall process seems to proceed through double kinetic resolution pathway but with the preferential transformation of each of the enantiomers at different stages. Regarding the encouraging results obtained in the preliminary experiments, further studies were conducted in order to develop the optimal reaction conditions for DKR process (Table 1).

The analysis of the data collected in Table 1 allows to draw one main conclusion – the diastereomeric excess of the product is affected by different conditions to a very small extent. In most of cases, the ratio of diasteromers is close to 3:1. On the other hand, the yield of the products

varied more. The reaction performed at low temperature afforded a product with lower yield (Table 1, entry 3). Organolithium bases worked well, but those derived from amines were either less effective (entry 7) or failed to give any product at all (entry 9). Sodium hydride was also less effective compared to the best performing bases (entry 8). It was also found that the use of less polar solvents resulted in a decrease of the product yields (entries 10 and 11).

Table 1 Optimization of Transesterification of *rac*-**3** with L-Menthoxide

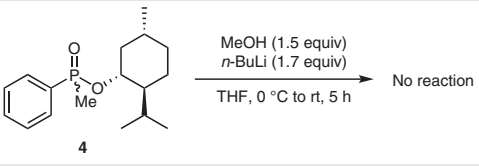


Entry	Deviation from standard conditions (equiv)	Conv.[a]	dr[a]
1	standard conditions[b]	73%	73:27 (S_P)
2	–78 to 0 °C	78%	76.5:23.5 (S_P)
3	–78 °C	58%	72:28 (S_P)
4	*s*-BuLi (1.1)	72%	71.5:28.5 (S_P)
5	*t*-BuLi (1.1)	77%	73:27 (S_P)
6	PhLi (1.1)	72%	72.5:27.5 (S_P)
7	LDA (1.1)	65%	73:27 (S_P)
8	NaH (1.1)	48%	73:27 (S_P)
9	NaHMDS (1.1)	no reaction	
10	*t*-BuLi (1.1), Et_2O	50%	74.5:25.5 (S_P)
11	*t*-BuLi (1.1), toluene	64%	74:26 (S_P)
12	L-menthol (0.7)/*n*-BuLi (0.6)	57%	72.5:27.5 (S_P)
13	L-menthol (0.7)/*n*-BuLi (1.1)	69%	74.5:25.5 (S_P)
14	L-menthol (1.0)/*n*-BuLi (0.6)	58%	72.5:27.5 (S_P)
15	L-menthol (1.0)/*n*-BuLi (1.7)	98%	76:24 (S_P)
16	L-menthol (1.0)/*n*-BuLi (2.5)	98%	73.5:26.5 (S_P)
17	L-menthol (1.5)/*n*-BuLi (1.1)	88%	72.5:27.5 (S_P)
18	L-menthol (1.5)/*n*-BuLi (1.7)	98%	71:5:28.5 (S_P)

[a] Conversion and diastereomeric excess of product were estimated based on ^{31}P NMR spectra of the reaction mixture.
[b] Standard conditions: L-menthol (1.0 equiv)/*n*-BuLi (1.1 equiv), THF, –78 °C to r.t., 5 h.

A set of reactions with different reactant stoichiometry were performed in the next stage (Table 1, entries 12–18). Based on these results it can be concluded that transesterification is generally very efficient and the only limit is the amount of either chiral alcohol or a base. But, irrespective of the conditions used, transesterification of **3** afforded product with similar diastereoselectivity level (43–52% de). This suggests that the efficiency of DKR process is affected mainly by the structures of chiral alcohol and phosphinic ester.

Another possible factor influencing the final outcome is the reversibility of the reaction. In this case, L-menthyl ester **4** could undergo transesterification with methoxide affording **3**. Different ratios of methanolysis for both diastereomers of **4** may lead to an enrichment of the latter in one diastereomer. It was decided therefore to submit **4** to a reaction with MeOLi (Scheme 3).



Scheme 3 Methanolysis of **4**

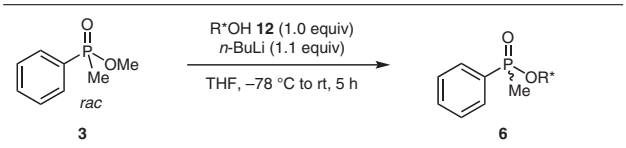
Under the standard reaction conditions, compound **4** remained unreactive towards MeO anion, which suggests that the selectivity of the reaction between **3** and L-menthoxide is shifted completely towards the product. In the literature, replacement of menthoxy group in **4** requires the use of very strong nucleophiles (amide anions[17] or organometallic reagents[18]) so the observed lack of reactivity of **4** towards MeO anion fits the literature data. Similarly, a reaction of diasteremerically enriched **4** with lithium L-menthoxide failed to give any changes in diastereomeric excess which suggests that, once formed, L-menthyl phosphinate **4** remains intact towards a chiral alkoxy anion.

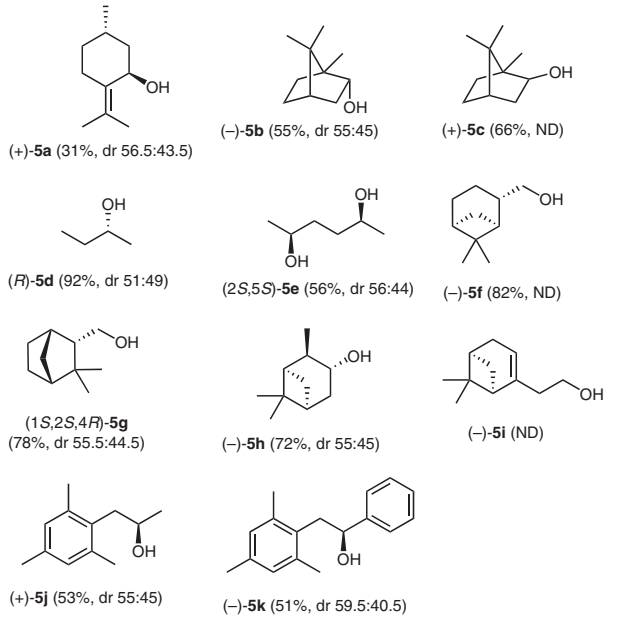
L-Menthol, chosen as a model chiral alcohol for DKR of racemic phosphinic acid ester **3**, led to some enrichment of the product. Therefore, in the next step a search for more efficient chiral alcohol was undertaken (Table 2).

The main conclusion that can be drawn from the data presented in Table 2 is that L-menthol is the most efficient chiral alcohol from all tested in the model reaction. It seems that noncyclic alcohols, as well as primary alcohols, are inefficient nucleophiles for DKR process. Moreover, bicyclic chiral alcohols, where the side differentiation is very clear, afforded the corresponding diastereomeric esters with low diastereoselectivity. The most prominent example, however, was (+)-pulegol (**5a**), an alcohol structurally similar to L-menthol, which afforded the corresponding ester **6a** with low diastereoselectivity. This suggests that an effective chiral alcohol should possess a cyclic structure and an additional chirality center with a bulky substituent at the carbon atom adjacent to carbinolic carbon. The latter seems to be crucial as for structurally similar (+)-pulegol (**5a**) lacking chirality center at nearby carbinolic carbon the selectivity of the process dropped dramatically.

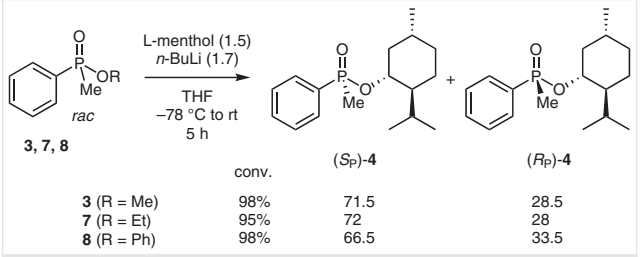
The ratio of the formed diastereomers may also be potentially influenced by the use of different leaving groups. It was therefore decided to check the stereoselectivity of transesterification of three different phosphinic esters (Scheme 4).

Table 2 The Search for the Best-Performing Chiral Alcohol[a]





[a] Conversion and diastereomeric excess of product was estimated based on ^{31}P NMR spectra of reaction mixture. ND: Not determined.

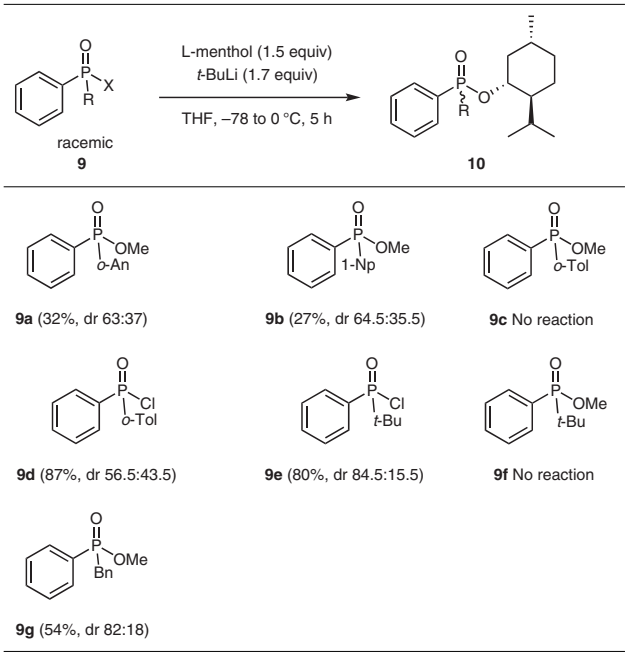


Scheme 4 The influence of leaving group on DKR process

In every case, transesterification of the substrate proceeded efficiently but the diastereoselectivity of the process varied to some degree and was the lowest for phenyl ester **8**. The highest value, on the other hand, was obtained with ethyl ester **7**, with a de value comparable with **3**. Based on the outcome it can be concluded that the nature of the leaving group may influence the selectivity of the process. This may be associated with either the lifetime of the intermediates or the direction of the addition. The lifetime of the intermediates is affected by pKa of the leaving group, so if the difference in the values for incoming and leaving group is small, the pentavalent intermediate should be stable enough to undergo Berry pseudorotation. On the other hand, the structure of the leaving group may influence the direction of the nucleophilic addition thus leading to the intermediates, which will need to undergo Berry pseudorotation prior to leaving group cleavage.

In the last step, it was decided to check the potential DKR for other organophosphorus electrophiles (Table 3).

Table 3 Substrate Scope in Transesterification Driven by DKR



It appeared that methyl diarylphosphinates **9a**,**b** underwent transesterification with L-menthol to a limited extent affording the corresponding L-menthyl esters with low diastereomeric excesses and for **9c** no reaction was observed at all. This might be ascribed to the higher crowding around phosphorus atom in the first approximation, but, a reaction of **9d** with L-menthol under the same reaction conditions does not support this thesis. In this case, esterification proceeded but the diastereoselectivity was low. This result, compared to the de value obtained for **9e**, lead to an assumption that both steric effects of different substituents at phosphorus and the nature of leaving group influence the DKR process. For **9e**, the crowding around phosphorus may force the chiral nucleophile to approach from a highly defined side, different for each enantiomer. This is not the case for **9d** where both less restricted approach along with the lability of the leaving group limits the lifetime of pentavalent intermediates and decreases the DKR effectiveness.

Unlike for carbon compounds, the stereochemistry of nucleophilic substitution in organophosphorus(V) compounds is less straightforward. The reason lies in a very specific two-step reaction pathway, which includes the formation of the corresponding pentavalent intermediate upon the attack of nucleophile at electrophilic phosphorus

atom in the first step. The nucleophilic attack occurs from the opposite side to one of the substituents (Figure 1), so, formally, four intermediates possessing trigonal bipyramidal structure should be obtained starting from one enantiomer.

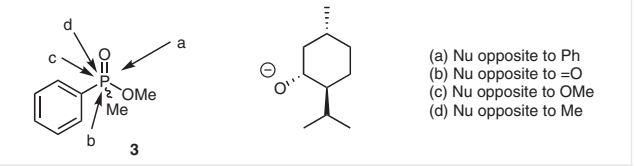


Figure 1 Possible nucleophilic attack of alkoxide at **3**

Bearing in mind that the substrate used in the discussed reaction is a racemate, the formation of the complex mixture of intermediates is expected unless the limited stability of pentavalent intermediates eliminates some of them. Moreover, depending on the relative reactions rates, Berry pseudorotation may be a competitive transformation, which in turn will have a great impact on the ratio of formed products.

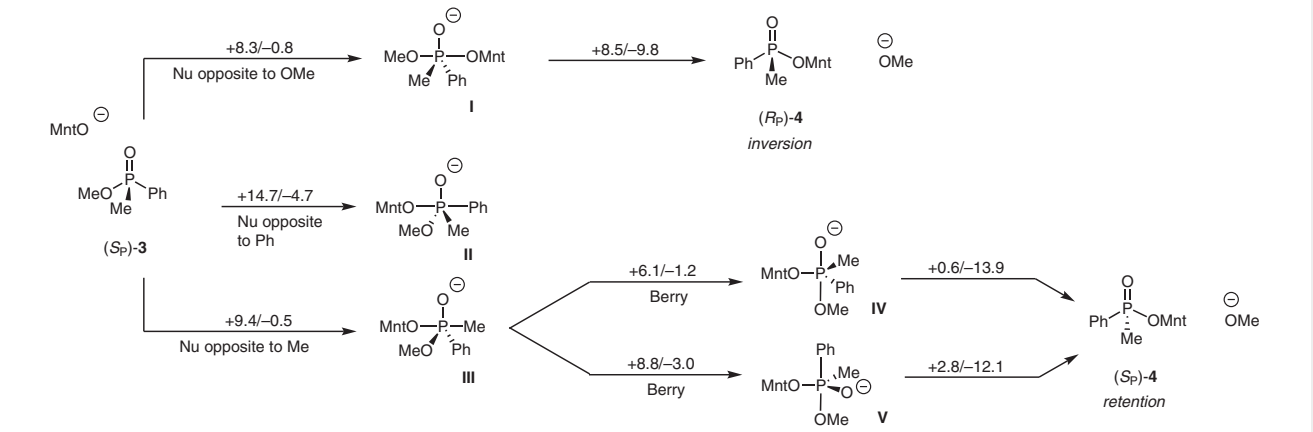
In order to understand the DKR phenomena in the studied transformation, DFT calculations of the reaction between both (S_P)-3 and L-menthoxide anion were carried out first (Scheme 5).

An interaction between (S_P)-**3** and lithium L-menthoxide proceeds through the initial formation of three associates where alkoxide points towards electrophilic phosphorus atom in between three substituents. The overall stabilization of these associates is similar and vary from –14.9 to –15.2 kcal/mol. In the next step, the incoming alkoxide undergoes bond formation with phosphorus atom leading to the corresponding pentavalent intermediate in cases where the nucleophile approaches opposite to MeO (**I**), Ph (**II**), and Me (**III**) but not when the nucleophile approaches apposite to O. The latter approach appeared to give unstable intermediate which spontaneously decomposes back to substrates. The analysis of activation/stabilization barriers for these three transformations [+8.3/–0.8 (for **I**), +14.7/–4.7 (for **II**), and +9.4/–0.5 (for **III**) kcal/mol, respectively] allow to highlight two dominant pathways for nucleophilic substitution in (S_P)-**3**. Intermediate **I** undergoes MeO group elimination affording the product with the overall inversion of configuration in a so called S_N@P process.[19] For **III**, direct MeO group elimination is impossible as only apically oriented groups are susceptible to cleavage from phosphorus.[20] Therefore, Berry pseudorotation must occur prior to elimination of MeO group. For **III**, this process can occur either via O and OMe or Ph and OMe shift towards apical positions. The first pseudorotation should afford intermediate **IV**, whereas the second will lead to **V**. Both intermediates may undergo OMe elimination affording the same product (S_P)-**4** with the formal retention of configuration at phosphorus.

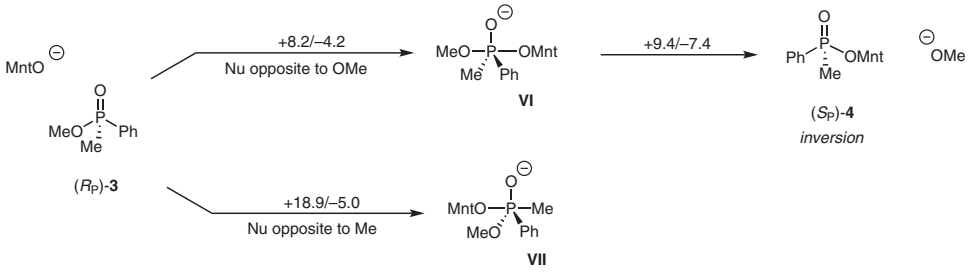
The most intriguing observation is associated with the activation energies for MeO dissociation in **I** and Berry pseudorotations of **III**. These values differ only slightly, which suggests that (S_P)-**3** undergoes nucleophilic substitution via two pathways leading to a mixture of diastereomers.

Similarly, DFT calculations of the reaction between (R_P)-**3** and L-menthoxide anion was also undertaken (Scheme 6).

Here, again, the formation of four associates is postulated but only two of them will undergo bond formation between electrophilic phosphorus atom and a chiral alkoxide according to DFT calculations. In the first case, the nucleophile approaches from the side opposite to MeO group affording **VI**, whereas in the second case the nucleophile approaches from the side opposite to Me group affording **VII**. The activation/stabilization energies are +8.2/–4.2 kcal/mol and +18.9/–5.0 kcal/mol for **VI** and **VII**, respectively. In contrast to (S_P)-**3**, the formation of a new bond between the nucleophile and phosphorus in (R_P)-**3** is remarkably dependent on the direction of the nucleophilic attack. The nucleophilic attack opposite to Ph group and oxygen failed to



Scheme 5 DFT analysis of nucleophilic substitution of (S_P)-**3** with L-menthoxide

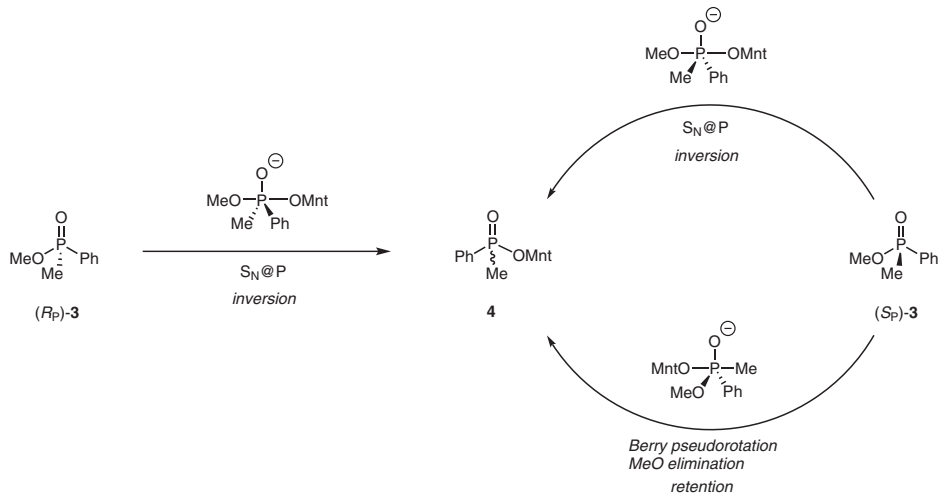


Scheme 6 DFT analysis of nucleophilic substitution of (R_P)-**3** with L-menthoxide

give stable pentavalent intermediates whereas the attack from the side opposite to methyl group, although possible, requires far higher activation energy compared to the attack from the side opposite to OMe group. It can be concluded here that for (R_P)-**3** the dominant process is S_N@P leading to a product with S_P configuration at phosphorus. As discussed above, for (S_P)-**3** two processes are operating with similar probability. The first is S_N@P leading to a product with R_P configuration at phosphorus and the second proceeding through a sequence: nucleophilic addition/Berry pseudorotation/leaving group cleavage. The latter process leads to the product with S_P configuration at phosphorus. Bearing in mind the activation energies for transformations of (S_P)-**3**, the formation of practically equimolar amounts of diastereomeric phosphinic esters **4** should be expected from this substrate. From this point the observed ratio of the products, which is close to 3:1, can be easily explained as a superposition of different reactivities of both enantiomers of **3** with the same chiral nucleophile. What is more interesting, DFT analysis predicts the formation of S_P diastereomer as the major reaction product. This was confirmed by the analysis of product mixture by NMR (^{1}H and ^{31}P) and a comparison with the literature data.[21] Based on these data it can be concluded also that the structure of the most effective chiral alcohol can be deduced based on the theoretical analysis of the initial reaction steps (P–O bond formation, Berry pseudorotation, and leaving group cleavage of the initial pentavalent intermediate) between a chiral alkoxide and phosphinic ester. This project is currently underway in the laboratory.

Both experimental and theoretical investigations allow to draw a general pathway for the transesterification of racemic phosphinic esters with chiral alkoxy anions (Scheme 7).

According to Scheme 7 above, each enantiomer of methyl ester **3** undergoes transformation into **4** in a different way. (R_P)-**3** reacts with L-menthoxide via simple S_N@P reaction where the incoming nucleophile approaches the electrophilic phosphorus from the side opposite to MeO group. This leads to the corresponding pentavalent intermediate, which undergoes MeO group cleavage affording the product with inversion of configuration at phosphorus. On the other hand, (S_P)-**3** reacts with the same nucleophile via two different mechanisms. The first includes simple S_N@P reaction similar to (R_P)-**3**, which leads to the product with inversion of configuration. Additionally, however, (S_P)-**3** reacts with L-menthoxide in a way where the incoming nucleophile attacks electrophilic phosphorus from the side



Scheme 7 Proposed transformation pathways of both enantiomers of **3** in the presence of L-menthoxide

opposite to Me group. In this case, the pentavalent intermediate is unable to undergo MeO group cleavage, which forces Berry pseudorotation to occur prior to MeO group cleavage. In this case, nucleophilic substitution proceeds with retention of configuration at phosphorus. For (S_P)-**3**, both pathways are equally possible as evidenced by DFT calculations. The above picture does not fit the classical definition of DKR process where racemic substrate undergoes equilibration into a chiral intermediate which then transforms into an enantioenriched product. Here, the same effect is obtained via different reactivity of two enantiomers of the substrate.

In conclusion, DKR of phosphinic esters with chiral alcohols in the presence of a base has been investigated. It appeared that a reaction of racemic methyl methylphenylphosphinate (**3**) with L-menthol in the presence of a base led to the formation of transesterified product in high yields and diastereomeric excess reaching 64% de. DFT calculations for this reaction were performed, which led to the conclusion that the process is not a classical dynamic kinetic resolution but a process where each enantiomer of the substrate undergoes transformation via different pathways. This observation has no literature precedent.

All reactions were performed under an argon atmosphere using Schlenk techniques. Only anhydrous solvents were used and the glassware was heated under vacuum prior to use. All chemicals were used as received unless otherwise noted. Solvents for chromatography and crystallization were distilled once before the use and the solvents for extraction were used as received. THF, toluene, and Et_2O were dried over sodium/benzophenone ketyl.

NMR spectra were recorded with Bruker Ascend (500 MHz) and Varian Mercury (400 MHz) spectrometers in $CDCl_3$ as a solvent at r.t., unless otherwise noted. Chemical shifts (δ) are reported in ppm relative to residual solvent peak. Mass spectra were recorded on Shimadzu GC-MS QP2010S spectrometer working in electron ionization (EI) mode using Phenomenex Zebron ZB-35HT INFERNO column (pressure: 65.0 kPa, total flow: 33.9 mL/min, column flow: 1.0 mL/min, linear velocity: 36.8 cm/sec, split: 30, temperature program (80 °C – hold 1 min, 80–300 °C/25 °C/min – hold 1 min, 300–340 °C/18 °C/min – hold 2 min: total 15 min). 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). (*R*)-Pulegol (**5a**),[22] *exo*-borneol (**5c**),[23] *cis*-myrtanol (**5f**),[24] *endo*-camphanol (**5g**),[24,25] (–)-isopinocampheol (**5h**),[24] (*R*)-1-mesitylpropan-2-ol (**5j**),[26] (*S*)-2–mesityl-1-phenylethanol (**5k**),[26,27] methyl methylphenylphosphinate,[12a] *o*-anisylphenylphosphine oxide,[28] *o*-tolylphenylphosphine oxide,[29] 1-naphthylphenylphosphine oxide,[30] benzylphenylphosphine oxide,[31] and *tert*-butylphenylphosphinic chloride (**9e**)[32] were prepared according to the literature procedures or were available from other research projects running in our laboratories. The preparation of compounds **7** and **8**, and details of the reaction of racemic **3** with chiral alcohols (Table 2) are provided in the Supporting Information.

Theoretical results presented in this work were obtained with the aid of the density functional theory (DFT) approach using B3LYP hybrid functional[33] in conjunction with the polarized valence triple zeta (VDZP) basis set 6-311++G**.[34,35] Incorporation of the diffuse functions (++) seems reasonable since some of the identified species are weakly bound complexes with significant distances between interacting molecules, and for this reason proper treatment of the electron density at large distances is desired. The calculations were carried out using the PQS quantum chemistry package.[36]

The geometry optimization for all the systems considered in this work was followed by the frequency calculations. Both minima and transition states (the first rank saddle points) were considered. In the case of minima all computed frequencies were real. On the other hand one imaginary frequency was obtained in the case of each transition state. Visual inspection of the corresponding Eigenmode allowed us to recognize species on each side of a transition state. The obtained energies were then used to calculate energy changes and barriers. All the reported energies were corrected for the zero point vibrational energies (ZPVE).

Methyl *tert*-Butylphenylphosphinate (9f)

In a flame-dried Schlenk tube equipped with magnetic stirrer and inert gas inlet, anhyd THF (10 mL) and MeOH (0.392 mL, 9.7 mmol) were placed and the mixture was cooled to –78 °C. A solution of *n*-BuLi (6.06 mL, 1.6 M) was added dropwise and after 15 min, a solution of *tert*-butylphenylphosphinic chloride (**9e**; 0.700 g, 3.2 mmol) in THF (5 mL) was slowly added. The reaction mixture was allowed to stir overnight at r.t. and then quenched with sat. aq NH_4Cl. The mixture was extracted with CH_2Cl_2 (3 × 10 mL), the combined organic layers were dried (Na_2SO_4), filtered, and evaporated. The residue was purified by column chromatography with EtOAc/MeOH (9:1) as eluent affording **9f** as a colorless oil; yield: 0.633 g (92%); R_f = 0.55 (EtOAc/MeOH 9:1); GC: t_R = 7.64 min.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.63–7.75 (m, 2 H), 7.50–7.55 (m, 1 H), 7.42–7.49 (m, 2 H), 3.65 (d, $J_{P,H}$ = 10.4 Hz, 3 H), 1.10 (d, $J_{P,H}$ = 15.8 Hz, 9 H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 133.2 (d, $J_{P,C}$ = 8.2 Hz), 132.0 (d, $J_{P,C}$ = 2.7 Hz), 128.2 (d, $J_{P,C}$ = 11.8 Hz), 127.8 (d, $J_{P,C}$ = 116.3 Hz), 51.5 (d, $J_{P,C}$ = 7.3 Hz), 32.5 (d, $J_{P,C}$ = 100.8 Hz), 24.2.

^{31}P NMR ($CDCl_3$, 202 MHz): δ = 52.8.

MS (EI, 70 eV): *m*/*z* (%) = 156 (100), 141 (51), 155 (17), 157 (11), 212 (8).

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{11}H_{17}O_2P$: 213.0966; found: 213.0967.

The data are in accordance with those previously reported in the literature.[37]

Phenyl(*o*-tolyl)phosphinic Chloride (9d)

H_2O_2 (30% w/w, 5 mL) was added dropwise to a suspension of phenyl(*o*-tolyl)phosphine oxide (0.225 g, 0.1 mmol) in aq 5 M NaOH (5 mL) at 90–100 °C and the mixture was stirred overnight at 100 °C. After the solution was cooled to 0 °C, concd HCl was added dropwise until precipitation of a white solid was no longer observed. The precipitate was collected by filtration and washed with H_2O and Et_2O, then dried in vacuo to give phenyl(*o*-tolyl)phosphinic acid (0.216 g), which was used in the next step without further purification.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 9.4 (br s, 1 H), 7.90–7.97 (m, 1 H), 7.65–7.72 (m, 2 H), 7.45–7.50 (m, 1 H), 7.34–7.43 (m, 3 H), 7.22–7.27 (m, 1 H), 7.14–7.19 (m, 1 H), 2.36 (s, 3 H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 141.6 (d, $J_{P,C}$ = 7.3 Hz), 133.0 (d, $J_{P,C}$ = 10.9 Hz), 132.3 (d, $J_{P,C}$ = 1.8 Hz), 131.8 (d, $J_{P,C}$ = 1.8 Hz), 131.3 (d,

$J_{P,C}$ = 1.8 Hz), 131.1 (d, $J_{P,C}$ = 10.9 Hz), 131.1 (d, $J_{P,C}$ = 137.2 Hz), 128.3 (d, $J_{P,C}$ = 13.6 Hz), 125.4 (d, $J_{P,C}$ = 13.6 Hz), 21.2 (d, $J_{P,C}$ = 3.6 Hz).

^{31}P NMR ($CDCl_3$, 202 MHz): δ = 35.1.

The data are in accordance with those previously reported in the literature.[38]

In a flame-dried and Schlenk tube equipped with magnetic stirrer and inert gas inlet phenyl(*o*-tolyl)phosphinic acid (0.203 g, 0.876 mmol) was placed followed by $SOCl_2$ (3 mL) at 0 °C. The reaction mixture was allowed to stir under reflux for 3 h. Subsequently, the $SOCl_2$ was removed under vacuum and the formed phosphinic chloride **9d** was used in next step without purification. Conversion according to ^{31}P NMR spectra of crude product was 100%.

^{31}P NMR (202 MHz, $CDCl_3$): δ = 46.4.

Methyl Phosphinate Esters; General Procedure

In a flame-dried Schlenk tube equipped with magnetic bar and inert gas inlet, secondary phosphine oxide (1.0 equiv) was placed followed by addition of CCl_4 (5 mL). Then the reaction mixture was cooled to 0 °C, and MeOH (2.0 equiv) and Et_3N (2.0 equiv) were added. The mixture was allowed to stir overnight at r.t. and then quenched with sat. aq NH_4Cl. The mixture was extracted with CH_2Cl_2 (3 × 10 mL), the combined organic layers were dried (Na_2SO_4), filtered, and evaporated. The residue was purified by column chromatography with EtOAc/MeOH (9:1) as eluent.

Methyl *o*-Anisylphenylphosphinate (9a)

Prepared according to the general procedure from *o*-anisylphenylphosphine oxide (0.233 g, 1.00 mmol), MeOH (0.082 mL, 2.01 mmol), and Et_3N (0.280 mL, 2.01 mmol); yield: 0.203 g (77%); white solid; mp 80.3–81.9 °C; R_f = 0.34 (EtOAc/MeOH 9:1); GC: t_R = 13.78 min.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.94–8.06 (m, 1 H), 7.79–7.91 (m, 2 H), 7.48–7.57 (m, 2 H), 7.39–7.48 (m, 2 H), 7.03–7.13 (m, 1 H), 6.87–6.91 (m, 1 H), 3.77 (d, $J_{P,H}$ = 11.4 Hz, 3 H), 3.73 (s, 3 H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 161.0 (d, $J_{P,C}$ = 3.6 Hz), 134.72 (d, $J_{P,C}$ = 3.6 Hz), 134.48 (d, $J_{P,C}$ = 2.7 Hz), 132.0 (d, $J_{P,C}$ = 142.6 Hz), 131.7 (d, $J_{P,C}$ = 9.1 Hz), 128.0 (d, $J_{P,C}$ = 13.6 Hz), 120.6 (d, $J_{P,C}$ = 12.7 Hz), 118.8 (d, $J_{P,C}$ = 136.2 Hz), 111.3 (d, $J_{P,C}$ = 8.2 Hz), 51.4 (d, $J_{P,C}$ = 5.5 Hz), 55.5.

^{31}P NMR ($CDCl_3$, 202 MHz): δ = 31.7.

MS (EI, 70 eV): *m*/*z* (%) = 263 (10), 262 (66), 261 (24), 244 (27), 233 (22), 231 (31), 229 (39), 212 (57), 199 (71), 171 (51), 155 (36), 91 (61), 77 (100).

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{15}O_3P$: 263.0828; found: 263.0832.

The data are in accordance with those previously reported in the literature.[39]

Methyl 1-Naphthylphenylphosphinate (9b)

Prepared according to the general procedure from 1-naphthylphenylphosphine oxide (0.508 g, 2.01 mmol), MeOH (0.163 mL, 4.03 mmol), and Et_3N (0.562 mL, 4.03 mmol); yield: 0.364 g (64%); brown-greenish oil; R_f = 0.58 (EtOAc/MeOH 9:1); GC: t_R = 16.02 min.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.50–8.55 (m, 1 H), 8.19–8.25 (m, 1 H), 8.04–8.07 (m, 1 H), 7.87–7.91 (m, 1 H), 7.79–7.85 (m, 2 H), 7.54–7.59 (m, 1 H), 7.49–7.54 (m, 3 H), 7.41–7.46 (m, 2 H), 3.84 (d, $J_{P,H}$ = 11.3 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 134.1 (d, $J_{P,C}$ = 9.1 Hz), 133.7 (d, $J_{P,C}$ = 10.0 Hz), 133.6 (d, $J_{P,C}$ = 2.7 Hz), 132.9 (d, $J_{P,C}$ = 11.8 Hz), 132.1 (d, $J_{P,C}$ = 2.7 Hz), 131.4 (d, $J_{P,C}$ = 10.9 Hz), 128.9, 128.5 (d, $J_{P,C}$ = 13.6 Hz), 127.5, 126.32, 126.29, 124.6 (d, $J_{P,C}$ = 14.5 Hz), 51.6 (d, $J_{P,C}$ = 6.4 Hz).

^{31}P NMR ($CDCl_3$, 202 MHz): δ = 34.6.

MS (EI, 70 eV): *m*/*z* (%) = 282 (37), 250 (16), 249 (93), 202 (16), 127 (19), 81 (100), 77 (20).

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{15}O_2P$: 283.0871; found: 283.0882.

The data are in accordance with those previously reported in the literature.[30]

Methyl Phenyl(*o*-tolyl)phosphinate (9c)

Prepared according to general procedure from phenyl(*o*-tolyl)phosphine oxide (0.233 g, 1.08 mmol), MeOH (0.087 mL, 2.16 mmol), and Et_3N (0.300 mL, 2.16 mmol); yield 0.228 g (86%); white crystals; mp 118.1–120.7 °C; R_f = 0.60 (EtOAc/MeOH 9:1); GC: t_R = 12.79 min.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.88–7.94 (m, 1 H), 7.73–7.79 (m, 2 H), 7.51–7.59 (m, 1 H), 7.40–7.51 (m, 3 H), 7.26–7.34 (m, 1 H), 7.15–7.26 (m, 1 H), 3.78 (d, $J_{P,H}$ = 11.0 Hz, 3 H), 2.44 (s, 3 H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 142.0 (d, $J_{P,C}$ = 11.8 Hz), 133.3 (d, $J_{P,C}$ = 9.1 Hz), 132.5 (d, $J_{P,C}$ = 2.7 Hz), 132.1 (d, $J_{P,C}$ = 2.7 Hz), 131.7 (d, $J_{P,C}$ = 10.0 Hz), 131.6 (d, $J_{P,C}$ = 134.4 Hz), 131.5 (d, $J_{P,C}$ = 12.7 Hz), 128.9 (d, $J_{P,C}$ = 134.4 Hz), 128.5 (d, $J_{P,C}$ = 12.7 Hz), 125.5 (d, $J_{P,C}$ = 12.7 Hz), 51.3 (d, $J_{P,C}$ = 6.4 Hz), 21.2 (d, $J_{P,C}$ = 3.6 Hz).

^{31}P NMR ($CDCl_3$, 202 MHz): δ = 34.0.

MS (EI, 70 eV): *m*/*z* (%) = 247 (10), 246 (68), 245 (100), 215 (18), 214 (13), 213 (70), 165 (27), 91 (19), 77 (20), 65 (14), 47 (11).

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{15}O_2P$: 247.0882; found: 247.0882.

The data are in accordance with those previously reported in the literature.[38]

Methyl Benzylphenylphosphinate (9g)

Prepared according to the general procedure from benzylphenylphosphine oxide (0.216 g, 1.00 mmol), MeOH (0.081 mL, 2.00 mmol), and Et_3N (0.278 mL, 2.00 mmol); yield: 0.204 g (83%); white solid; mp 79.3–82.0 °C; R_f = 0.37 (EtOAc/MeOH 9:1); GC: t_R = 10.84 min.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.56–7.63 (m, 2 H), 7.49–7.55 (m, 1 H), 7.38–7.44 (m, 2 H), 7.16–7.25 (m, 3 H), 7.07–7.12 (m, 2 H), 3.64 (d, $J_{P,H}$ = 11.0 Hz, 3 H), 3.30 (d, $J_{P,H}$ = 17.7 Hz, 2 H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 132.3 (d, $J_{P,C}$ = 2.7 Hz), 132.0 (d, $J_{P,C}$ = 10.0 Hz), 131.2 (d, $J_{P,C}$ = 7.3 Hz), 129.9 (d, $J_{P,C}$ = 5.5 Hz), 129.3 (d, $J_{P,C}$ = 125.3 Hz), 128.4 (d, $J_{P,C}$ = 10.9 Hz), 128.3, 126.7 (d, $J_{P,C}$ = 2.7 Hz), 51.4 (d, $J_{P,C}$ = 6.4 Hz), 37.7 (d, $J_{P,C}$ = 96.3 Hz).

^{31}P NMR ($CDCl_3$, 202 MHz): δ = 41.7.

MS (EI, 70 eV): *m*/*z* (%) = 246 (17), 245 (29), 168 (13), 156 (8), 155 (100), 91 (26).

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{15}O_2P$: 247.0877; found: 247.0882.

The data are in accordance with those previously reported in the literature.[40]

Transesterification of Phosphinic Derivatives with L-Menthol; General Procedure

In a flame-dried Schlenk tube equipped with magnetic stirrer and inert gas inlet, L-menthol (1.5 equiv) was placed followed by the addition of THF (3 mL). Then, the reaction mixture was cooled to –78 °C and solution of *t*-BuLi (1.7 equiv, 1.7 M) was added dropwise. The re-

action mixture was allowed to stir for 15 min, and the previously prepared solution of methyl phosphinate or phosphinic chloride (in 3 mL of THF) was slowly added. The reaction mixture was allowed to warm to r.t. and stirred for 5 h, then quenched with sat. aq NH_4Cl followed by extraction with CH_2Cl_2 (3 × 10 mL). The combined organic layers were dried (Na_2SO_4), filtered, and evaporated. The crude product was further purified by column chromatography.

L-Menthyl Methylphenylphosphinate (4; Mixture of Diastereomers)

Prepared according to the general procedure from methyl methylphenylphosphinate (**3**; 0.085 g, 0.50 mmol), L-menthol (0.117 g, 0.75 mmol), and *n*-BuLi (0.50 mL, 0.85 mmol); yield: 0.126 g (86%, 53% de); R_f = 0.54 (EtOAc/MeOH 9:1); GC: t_R = 12.87 min (minor), t_R = 12.92 min (major).

^{1}H NMR ($CDCl_3$, 500 MHz): δ (major) = 7.78–7.84 (m, 2 H), 7.52–7.57 (m, 1 H), 7.45–7.41 (m, 2 H), 3.93–4.01 (m, 1 H), 2.35–2.41 (m, 1 H), 1.88–1.96 (m, 1 H), 1.71 (d, $J_{P,H}$ = 14.5 Hz, 3 H), 1.55–1.63 (m, 2 H), 1.20–1.46 (m, 3 H), 0.80–1.05 (m, 2 H), 0.92 (d, $J_{P,H}$ = 6.3 Hz, 3 H), 0.82 (d, $J_{P,H}$ = 7.3 Hz, 3 H), 0.31 (d, $J_{P,H}$ = 6.9 Hz, 3 H); δ (minor) = 7.78–7.84 (m, 2 H), 7.52–7.57 (m, 1 H), 7.45–7.41 (m, 2 H), 4.25–4.33 (m, 1 H), 2.17–2.24 (m, 1 H), 1.79–1.85 (m, 1 H), 1.65 (d, $J_{P,H}$ = 14.2 Hz, 3 H), 1.55–1.63 (m, 2 H), 1.20–1.46 (m, 3 H), 0.80–1.05 (m, 2 H), 0.96 (d, $J_{P,H}$ = 6.9 Hz, 3 H), 0.89 (d, $J_{P,H}$ = 6.6 Hz, 3 H), 0.77 (d, $J_{P,H}$ = 6.6 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ (major) = 132.0 (d, $J_{P,C}$ = 2.7 Hz), 131.1 (d, $J_{P,C}$ = 10.0 Hz), 128.4 (d, $J_{P,C}$ = 12.7 Hz), 48.7, 43.9, 34.1, 31.5, 25.4, 22.7, 22.0, 21.1, 16.5 (d, $J_{P,C}$ = 102.6 Hz), 15.2; δ (minor) = 131.9 (d, $J_{P,C}$ = 2.7 Hz), 130.8 (d, $J_{P,C}$ = 10.9 Hz), 128.4 (d, $J_{P,C}$ = 12.7 Hz), 48.8, 43.2, 34.1, 31.4, 25.9, 23.0, 21.9, 21.1, 16.5 (d, $J_{P,C}$ = 102.6 Hz), 15.8.

^{31}P NMR ($CDCl_3$, 202 MHz): δ (major) = 40.5; δ (minor) = 39.8.

MS (EI, 70 eV): *m*/*z* (%) = 158 (8), 157 (100), 139 (15), 95 (10), 81 (8), 79 (9), 77 (6), 55 (6).

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{27}O_2P$: 295.1820; found: 295.1821.

The data are in accordance with those previously reported in the literature.[41]

L-Menthyl (*o*-Anisyl)phenylphosphinate (17a; Mixture of Diastereomers)

Prepared according to the general procedure from methyl *o*-anisylphenylphosphinate (**9a**; 0.129 g, 0.49 mmol), L-menthol (0.116 g, 0.74 mmol), and *n*-BuLi (0.49 mL, 0.84 mmol); yield: 0.061 g (32%, 26% de); R_f = 0.61 (EtOAc/MeOH 9:1); GC: t_R = 13.65 min.

^{1}H NMR ($CDCl_3$, 500 MHz): δ (major) = 8.04–8.10 (m, 1 H), 7.80–7.87 (m, 2 H), 7.46–7.53 (m, 2 H), 7.38–7.44 (m, 2 H), 7.05–7.10 (m, 1 H), 6.82–6.86 (m, 1 H), 4.21–4.31 (m, 1 H), 3.63 (s, 3 H), 2.13–2.24 (m, 1 H), 1.60–1.69 (m, 1 H), 1.33–1.51 (m, 3 H), 1.19–1.31 (m, 2 H), 0.83–1.02 (m, 2 H), 0.89 (d, $J_{P,H}$ = 6.6 Hz, 3 H), 0.86 (d, $J_{P,H}$ = 6.3 Hz, 3 H), 0.50 (d, $J_{P,H}$ = 6.9 Hz, 3 H); δ (minor) = 8.00–8.05 (m, 1 H), 7.80–7.87 (m, 2 H), 7.46–7.53 (m, 2 H), 7.38–7.44 (m, 2 H), 7.05–7.10 (m, 1 H), 6.86–6.89 (m, 1 H), 4.21–4.31 (m, 1 H), 3.68 (s, 3 H), 2.13–2.24 (m, 1 H), 1.60–1.69 (m, 1 H), 1.33–1.51 (m, 3 H), 1.19–1.31 (m, 2 H), 0.83–1.02 (m, 2 H), 0.88 (d, $J_{P,H}$ = 6.3 Hz, 3 H), 0.86 (d, $J_{P,H}$ = 6.3 Hz, 3 H), 0.55 (d, $J_{P,H}$ = 6.9 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ (major) = 160.8 (d, $J_{P,C}$ = 4.5 Hz), 134.8 (d, $J_{P,C}$ = 6.4 Hz), 134.1 (d, $J_{P,C}$ = 1.8 Hz), 131.5 (d, $J_{P,C}$ = 10.9 Hz), 131.2 (d, $J_{P,C}$ = 2.7 Hz), 127.7 (d, $J_{P,C}$ = 13.6 Hz), 120.4 (d, $J_{P,C}$ = 12.7 Hz), 110.9 (d, $J_{P,C}$ = 8.2 Hz), 55.0, 48.9, 43.8, 34.1, 31.6, 25.2, 22.7, 22.0, 21.2, 15.2; δ (minor) = 161.1 (d, $J_{P,C}$ = 4.5 Hz), 134.4 (d, $J_{P,C}$ = 6.4 Hz), 134.0 (d, $J_{P,C}$ = 1.8 Hz), 131.4 (d, $J_{P,C}$ = 10.0 Hz), 131.3 (d, $J_{P,C}$ = 2.7 Hz), 127.8 (d, $J_{P,C}$ = 13.6 Hz), 120.5 (d, $J_{P,C}$ = 12.7 Hz), 111.3 (d, $J_{P,C}$ = 7.3 Hz), 55.3, 48.9, 43.2, 34.1, 31.5, 25.4, 22.7, 22.0, 21.2, 15.3.

^{31}P NMR ($CDCl_3$, 202 MHz): δ (major) = 27.8; δ (minor) = 27.4.

MS (EI, 70 eV): *m*/*z* (%) = 279 (19), 262 (6), 261 (66), 167 (52), 150 (12), 149 (100), 121 (22), 113 (22), 112 (83), 104 (25), 95 (11), 84 (40), 83 (54), 82 (14).

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{23}H_{31}O_3P$: 387.2091; found: 387.2084.

The data are in accordance with those previously reported in the literature.[41]

L-Menthyl (1-Naphthyl)phenylphosphinate (17b; Mixture of Diastereomers)

Prepared according to the general procedure from methyl 1-naphthylphenylphosphinate (**9b**; 0.139 g, 0.49 mmol), L-menthol (0.115 g, 0.74 mmol), and *n*-BuLi (0.49 mL, 0.84 mmol); yield: 0.054 g (27%, 29% de); R_f = 0.57 (EtOAc/MeOH 9:1); GC: t_R = 13.64 min.

^{1}H NMR ($CDCl_3$, 500 MHz): δ (major) = 8.44–8.47 (m, 1 H), 8.27–8.35 (m, 1 H), 8.03–8.06 (m, 1 H), 7.75–7.88 (m, 3 H), 7.55–7.62 (m, 1 H), 7.40–7.51 (m, 5 H), 4.37–4.50 (m, 1 H), 2.13–2.16 (m, 1 H), 1.91–2.04 (m, 1 H), 1.59–1.71 (m, 2 H), 1.33–1.52 (m, 2 H), 1.13–1.23 (m, 1 H), 0.81–1.02 (m, 2 H), 0.87 (d, $J_{P,H}$ = 6.3 Hz, 3 H), 0.86 (d, $J_{P,H}$ = 6.9 Hz, 3 H), 0.41 (d, $J_{P,H}$ = 6.9 Hz, 3 H); δ (minor) = 8.44–8.47 (m, 1 H), 8.27–8.35 (m, 1 H), 8.03–8.06 (m, 1 H), 7.75–7.88 (m, 3 H), 7.55–7.62 (m, 1 H), 7.40–7.51 (m, 5 H), 4.37–4.50 (m, 1 H), 2.13–2.16 (m, 1 H), 1.91–2.04 (m, 1 H), 1.59–1.71 (m, 2 H), 1.33–1.52 (m, 2 H), 1.13–1.23 (m, 1 H), 0.81–1.02 (m, 2 H), 0.87 (d, $J_{P,H}$ = 6.3 Hz, 3 H), 0.86 (d, $J_{P,H}$ = 6.9 Hz, 3 H), 0.76 (d, $J_{P,H}$ = 6.9 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ (major) = 134.2 ($J_{P,C}$ = 137 Hz), 133.7, 133.6 ($J_{P,C}$ = 11.0 Hz), 133.3 ($J_{P,C}$ = 3.3 Hz), 132.8 ($J_{P,C}$ = 11.6 Hz), 131.7 ($J_{P,C}$ = 2.7 Hz), 131.2 ($J_{P,C}$ = 11.0 Hz), 128.7 ($J_{P,C}$ = 1.1 Hz), 128.3 ($J_{P,C}$ = 13.3 Hz), 127.1 ($J_{P,C}$ = 134 Hz), 127.0, 126.8 ($J_{P,C}$ = 4.9 Hz), 126.1, 124.6 ($J_{P,C}$ = 14.4 Hz), 77.3 ($J_{P,C}$ = 6.6 Hz), 48.8 (d, $J_{P,C}$ = 6.0 Hz), 43.6, 34.0, 31.5, 25.3, 22.7, 22.0, 21.0, 15.1; δ (minor) = 134.2 ($J_{P,C}$ = 137 Hz), 133.7, 133.6 ($J_{P,C}$ = 11.0 Hz), 133.3 ($J_{P,C}$ = 3.3 Hz), 132.8 ($J_{P,C}$ = 11.6 Hz), 131.7 ($J_{P,C}$ = 2.7 Hz), 131.2 ($J_{P,C}$ = 11.0 Hz), 128.7 ($J_{P,C}$ = 1.1 Hz), 128.3 ($J_{P,C}$ = 13.3 Hz), 128.1 ($J_{P,C}$ = 134 Hz), 126.9, 126.7 ($J_{P,C}$ = 4.9 Hz), 126.1, 124.5 ($J_{P,C}$ = 14.4 Hz), 77.3 ($J_{P,C}$ = 6.6 Hz), 48.8 (d, $J_{P,C}$ = 6.0 Hz), 43.6, 34.0, 31.5, 25.3, 22.7, 22.0, 21.0, 15.1.

^{31}P NMR ($CDCl_3$, 202 MHz): δ (major) = 29.6; δ (minor) = 29.4.

MS (EI, 70 eV): *m*/*z* (%) = 279 (18), 262 (12), 261 (69), 167 (55), 150 (12), 149 (100), 121 (22), 113 (26), 112 (94), 104 (24), 84 (43), 83 (60), 82 (15).

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{26}H_{31}O_2P$: 429.1959; found: 429.1954.

The data are in accordance with those previously reported in the literature.[21]

L-Menthyl Phenyl(*o*-tolyl)phosphinate (17c; Mixture of Diastereomers)

Prepared according to the general procedure from phenyl(*o*-tolyl)phosphinic chloride (**9d**; 0.251 g, 1.00 mmol), L-menthol (0.235 g, 1.50 mmol), and *n*-BuLi (1.00 mL, 1.70 mmol); yield: 0.323 g (87%, 13% de); R_f = 0.55 (hexane/acetone 3:1); GC: t_R = 13.75 min (major) and t_R = 13.87 min (minor).

^{1}H NMR ($CDCl_3$, 500 MHz): δ (major) = 8.02–8.09 (m, 1 H), 7.68–7.79 (m, 2 H), 7.47–7.53 (m, 1 H), 7.39–7.46 (m, 3 H), 7.30–7.35 (m, 1 H), 7.16–7.22 (m, 1 H), 4.31–4.37 (m, 1 H), 2.46–2.53 (m, 1 H), 2.34 (s, 3

H), 2.13–2.16 (m, 1 H), 1.89–1.92 (m, 1 H), 1.64–1.70 (m, 2 H), 1.36–1.50 (m, 1 H), 1.18–1.28 (m, 1 H), 0.75–1.02 (m, 2 H), 0.93 (d, $J_{P,H}$ = 6.0 Hz, 3 H), 0.88 (d, $J_{P,H}$ = 6.6 Hz, 3 H), 0.47 (d, $J_{P,H}$ = 6.9 Hz, 3 H); δ (minor) = 8.02–8.09 (m, 1 H), 7.68–7.79 (m, 2 H), 7.47–7.53 (m, 1 H), 7.39–7.46 (m, 3 H), 7.30–7.35 (m, 1 H), 7.16–7.22 (m, 1 H), 4.38–4.39 (m, 1 H), 2.36 (s, 3 H), 2.25–2.28 (m, 1 H), 1.89–1.92 (m, 1 H), 1.64–1.70 (m, 3 H), 1.36–1.50 (m, 1 H), 1.18–1.28 (m, 1 H), 0.75–1.02 (m, 2 H), 0.95 (d, $J_{P,H}$ = 7.3 Hz, 3 H), 0.83 (d, $J_{P,H}$ = 6.0 Hz, 3 H), 0.67 (d, $J_{P,H}$ = 6.3 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ (major) = 141.6 (d, $J_{P,C}$ = 12.7 Hz), 134.1 (d, $J_{P,C}$ = 132.6 Hz), 132.8 (d, $J_{P,C}$ = 8.2 Hz), 132.0 (d, $J_{P,C}$ = 2.7 Hz), 131.6 (d, $J_{P,C}$ = 2.7 Hz), 131.4 (d, $J_{P,C}$ = 10.9 Hz), 131.3 (d, $J_{P,C}$ = 11.8 Hz), 130.4 (d, $J_{P,C}$ = 136.2 Hz), 128.3, 128.2 (d, $J_{P,C}$ = 11.8 Hz), 125.3 (d, $J_{P,C}$ = 12.7 Hz), 48.8, 43.7, 34.0, 31.5, 25.4, 22.6, 21.9, 21.3, 21.0, 15.2; δ (minor) = 141.9 (d, $J_{P,C}$ = 12.7 Hz), 133.0 (d, $J_{P,C}$ = 133.5 Hz), 132.9 (d, $J_{P,C}$ = 8.2 Hz), 132.1 (d, $J_{P,C}$ = 2.7 Hz), 131.7 (d, $J_{P,C}$ = 2.7 Hz), 131.4 (d, $J_{P,C}$ = 10.9 Hz), 131.3 (d, $J_{P,C}$ = 11.8 Hz), 130.7 (d, $J_{P,C}$ = 136.2 Hz), 128.3, 128.2 (d, $J_{P,C}$ = 11.8 Hz), 125.3 (d, $J_{P,C}$ = 12.7 Hz), 48.8, 43.7, 34.0, 31.5, 25.4, 22.6, 21.9, 21.3, 21.0, 15.2.

^{31}P NMR ($CDCl_3$, 202 MHz): δ (major) = 29.4; δ (minor) = 28.8.

MS (EI, 70 eV): *m*/*z* (%) = 234 (14), 233 (100), 232 (59), 231 (56), 215 (11), 213 (9), 165 (8), 141 (8), 95 (11), 91 (8), 81 (8).

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{23}H_{31}O_2P$: 371.2127; found: 371.2134.

L-Menthyl *tert*-Butylphenylphosphinate (17d; Mixture of Diastereomers)

Prepared according to the general procedure from *tert*-butylphenylphosphinic chloride (**9e**; 0.108 g, 0.50 mmol), L-menthol (0.117 g, 0.75 mmol), and *n*-BuLi (0.50 mL, 0.85 mmol); yield: 0.134 g (80%, 69% de); R_f = 0.71 (EtOAc/hexane 9:1); GC: t_R = 13.16 min (major) and t_R = 13.21 min (minor).

^{1}H NMR ($CDCl_3$, 500 MHz): δ (major) = 7.77–7.85 (m, 2 H), 7.50–7.56 (m, 1 H), 7.42–7.48 (m, 2 H), 4.01–4.10 (m, 1 H), 2.46–2.53 (m, 1 H), 2.11–2.21 (m, 1 H), 1.72–1.83 (m, 1 H), 1.57–1.70 (m, 2 H), 1.35–1.49 (m, 1 H), 1.18–1.28 (m, 1 H), 1.13 (d, $J_{P,H}$ = 15.5 Hz, 9 H), 0.75–1.04 (m, 2 H), 0.90 (d, $J_{P,H}$ = 6.0 Hz, 3 H), 0.89 (d, $J_{P,H}$ = 6.6 Hz, 3 H), 0.48 (d, $J_{P,H}$ = 6.9 Hz, 3 H); δ (minor) = 7.77–7.85 (m, 2 H), 7.50–7.56 (m, 1 H), 7.42–7.48 (m, 2 H), 4.29–4.37 (m, 1 H), 2.36–2.44 (m, 1 H), 1.72–1.83 (m, 1 H), 1.57–1.70 (m, 3 H), 1.35–1.49 (m, 1 H), 1.18–1.28 (m, 1 H), 1.11 (d, $J_{P,H}$ = 12.9 Hz, 9 H), 0.75–1.04 (m, 2 H), 0.97 (d, $J_{P,H}$ = 7.3 Hz, 3 H), 0.87 (d, $J_{P,H}$ = 6.0 Hz, 3 H), 0.71 (d, $J_{P,H}$ = 6.3 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ (major) = 133.2 (d, $J_{P,C}$ = 8.2 Hz), 131.8 (d, $J_{P,C}$ = 2.7 Hz), 129.4 (d, $J_{P,C}$ = 113.5 Hz), 127.9 (d, $J_{P,C}$ = 10.9 Hz), 55.0, 49.1, 43.8, 34.1, 32.9 (d, $J_{P,C}$ = 101.7 Hz), 31.6, 25.4, 24.4, 22.6, 22.0, 21.2, 15.4; δ (minor) = 133.2 (d, $J_{P,C}$ = 8.2 Hz), 131.6 (d, $J_{P,C}$ = 2.7 Hz), 129.4 (d, $J_{P,C}$ = 113.5 Hz), 127.9 (d, $J_{P,C}$ = 10.9 Hz), 49.1, 43.2, 34.1, 32.9 (d, $J_{P,C}$ = 101.7 Hz), 31.4, 25.4, 24.4, 22.6, 21.9, 21.2, 15.4.

^{31}P NMR ($CDCl_3$, 202 MHz): δ (major) = 48.4; δ (minor) = 47.6.

MS (EI, 70 eV): *m*/*z* (%) = 200 (11), 199 (100), 143 (19), 142 (12), 139 (11), 95 (11), 83 (37), 81 (13), 57 (19), 55 (16).

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{33}O_2P$: 337.2295; found: 337.2291.

The data are in accordance with those previously reported in the literature.[41]

L-Menthyl Benzylphenylphosphinate (17e; Mixture of Diastereomers)

Prepared according to the general procedure from methyl benzylphenylphosphinate (**9g**; 0.122 g, 0.49 mmol), L-menthol (0.116 g, 0.74 mmol), and *n*-BuLi (0.49 mL, 0.84 mmol); yield: 0.099 g (54%, 64% de); R_f = 0.67 (EtOAc/hexane 9:1); GC: t_R = 13.76 min (major) and t_R = 13.87 min (minor).

^{1}H NMR ($CDCl_3$, 500 MHz): δ (major) = 7.61–7.69 (m, 2 H), 7.46–7.53 (m, 1 H), 7.36–7.43 (m, 2 H), 7.17–7.25 (m, 3 H), 7.10–7.17 (m, 2 H), 3.98–4.07 (m, 1 H), 3.32 (d, $J_{P,H}$ = 17.7 Hz, 2 H), 2.15–2.22 (m, 1 H), 1.87–1.94 (m, 1 H), 1.56–1.63 (m, 2 H), 1.29–1.40 (m, 2 H), 1.10–1.20 (m, 1 H), 0.76–1.02 (m, 2 H), 0.87 (d, $J_{P,H}$ = 6.3 Hz, 3 H), 0.81 (d, $J_{P,H}$ = 7.3 Hz, 3 H), 0.37 (d, $J_{P,H}$ = 6.9 Hz, 3 H); δ (minor) = 7.61–7.69 (m, 2 H), 7.46–7.53 (m, 1 H), 7.36–7.43 (m, 2 H), 7.17–7.25 (m, 3 H), 7.10–7.17 (m, 2 H), 4.24–4.33 (m, 1 H), 3.24 (dd, $J_{H,H}$ = 9.1 Hz, $J_{P,H}$ = 17.0 Hz, 2 H), 2.32–2.36 (m, 1 H), 1.95–2.00 (m, 1 H), 1.70–1.76 (m, 2 H), 1.29–1.40 (m, 2 H), 1.10–1.20 (m, 1 H), 0.76–1.02 (m, 2 H), 0.87 (d, $J_{P,H}$ = 7.3 Hz, 3 H), 0.81 (d, $J_{P,H}$ = 7.3 Hz, 3 H), 0.73 (d, $J_{P,H}$ = 6.3 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ (major) = 132.0 (d, $J_{P,C}$ = 10.6 Hz), 131.8 (d, $J_{P,C}$ = 7.7 Hz), 130.14 (d, $J_{P,C}$ = 5.4 Hz), 130.08 (d, $J_{P,C}$ = 2.7 Hz), 128.2, 128.1 (d, $J_{P,C}$ = 14.2 Hz), 126.6 (d, $J_{P,C}$ = 6.4 Hz), 48.8, 43.7, 38.8 (d, $J_{P,C}$ = 97.2 Hz), 34.0, 31.5, 25.4, 22.6, 21.9, 21.0, 15.2; δ (minor) = 132.0 (d, $J_{P,C}$ = 10.6 Hz), 131.8 (d, $J_{P,C}$ = 7.7 Hz), 130.14 (d, $J_{P,C}$ = 5.4 Hz), 130.08 (d, $J_{P,C}$ = 2.7 Hz), 128.2, 128.1 (d, $J_{P,C}$ = 14.2 Hz), 126.6 (d, $J_{P,C}$ = 6.4 Hz), 48.8, 43.1, 38.8 (d, $J_{P,C}$ = 97.2 Hz), 34.0, 31.4, 25.4, 22.7, 21.9, 21.0, 15.5.

^{31}P NMR ($CDCl_3$, 202 MHz): δ (major) = 37.8; δ (minor) = 37.1.

MS (EI, 70 eV): *m*/*z* (%) = 234 (14), 233 (100), 232 (59), 231 (56), 215 (11), 213 (9), 165 (8), 141 (8), 95 (11), 91 (8), 81 (8).

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{31}O_2P$: 393.1944; found: 393.1954.

The data are in accordance with those previously reported in the literature.[42]

Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0037-1609947.

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