Silver-Catalyzed Regioselective Phosphorylation of *para*-Quinone Methides with P(III)-Nucleophiles

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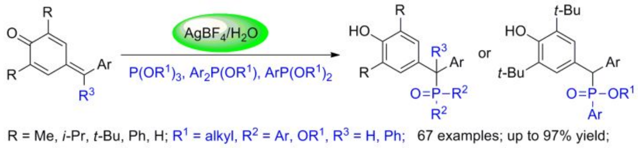
Abstract

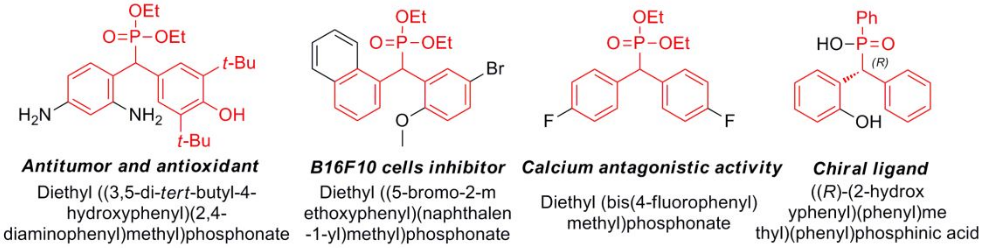


A simple and efficient method for the silver-catalyzed regioselective phosphorylation of *para*-quinone methides (*p*-QMs) with P(III)-nucleophiles ($P(OR)_3$, $ArP(OR)_2$, Ar_2P-OR) has been established via Michaelis-Arbuzov-type reaction. A broad range of P(III)-nucleophiles and *para*-quinone methides are well tolerated under the mild conditions, giving the expected diarylmethyl-substituted organophosphorus compounds with good to excellent yields. Moreover, a series of corresponding enantiomers can be obtained by employing dialkyl arylphosphonite ($ArP(OR)_2$) as substrates. The control experiments and ^{31}P-NMR tracking experiments were also performed to gain the insights for the plausible reaction mechanism. This protocol may have significant implications for the formation of C(sp^3)-P bonds in Michaelis-Arbuzov-type reaction.

Introduction

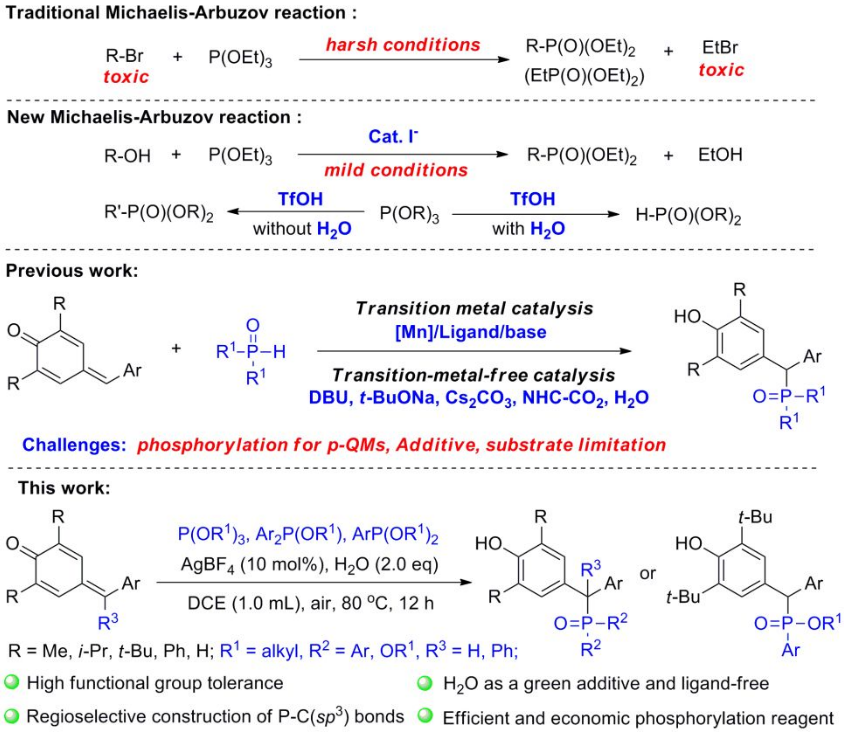
Organophosphorus compounds are widely used in organic synthesis, materials chemistry, homogeneous catalysis, coordination chemistry and medicinal chemistry.[1] Additionally, the construction of the C(sp^3)-P bonds for the synthesis and applications of α-diarylmethyl-substituted organophosphorus compounds is of great interest in organic synthesis and pharmaceutical industry (**Scheme 1**).[2] The traditional methods for the synthesis of these compounds generally involve the use of Michaelis-Becker reaction or Michaelis-Arbuzov by employing alkyl halides and phosphites as substrates.[3] In addition, the transition-metal-catalyzed cross-coupling reaction between aryl halides and benzyl phosphonates is also an attractive route for the synthesis of these compounds.[4] However, it is obvious that these famous reactions have some drawbacks, such as the use of toxic of the starting material and high temperature, which can cause the reaction with low atom efficiency and selectivity, bad functional group tolerance and the corresponding environmental problems.

Scheme 1. Important α-diarylmethyl-substituted organophosphorus compounds.



The classical Michaelis-Arbuzov reaction is extensively employed in industry and labratory for the generation of high-value organophosphorus compounds every year. According to Pearson's Hard-Soft-Acid-Base (HSBA) theory, P(III)-nucleophiles are typical soft bases, which have been widely used as efficient phosphorylation reagent in organic synthesis.[5] In addition, hydrogen phosphonates H-P(O)(OR)$_2$ are usually prepared from the reactions of PCl$_3$ and ROH (2.0 equiv) via hydrolysis and reduced pressure distillation, which shows the drawbacks of high energy consumption, equipment corrosions and poor reaction selectivity. Therefore, from the view point of economic and green chemistry, phosphites P(OR)$_3$ are more reasonable to be used as the raw materials. In 2017, Kang *et al.* reported the synthesis of *N*-heterocyclic phosphorodiamidic acids (NHPAs), which could be employed as an efficient Brønsted acid in phospha-Michael addition reaction for the synthesis of diaryl phosphonates.[6] In addition, Butkevich et al. investigated the direct nucleophilic addition of P(III)-nucleophiles to highly polarized or cationic fluorophores for the construction of P-C(sp^3) bonds with the assistance of an oxidant.[7] Very recently, Lei and coworkers studied the electrochemical oxidative C-H phosphorylation of 2-phenylimidazo[1,2-a]pyridine derivatives with phosphites. The reaction was performed under an exogenous-oxidant-free and transition-metal-free electrochemical oxidation conditions, giving the significant organophosphorus compounds with moderate to high yields, accompanied by the evolution of hydrogen.[8]

Scheme 2. Methods for the synthesis of α-diarylmethyl organophosphorus compounds.

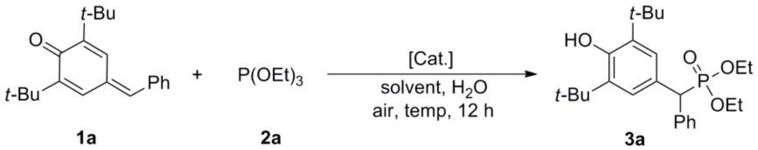


para-Quinone methides (*p*-QMs), which have been widely used as electron-deficient alkenes in organic synthesis, especially in the intermolecular cyclization transformations and 1,6-conjugated addition because of their intrinsic reactivities.[9-12] In 2016, the *N*-heterocyclic carbene catalyzed 1,6-hydrophosphorylation of fuchsones and *para*-quinone methides with dialkyl phosphonates was achieved by Anand *et al*., a variety of unsymmetrical triarylmethyl phosphonates were synthesized in moderate yields.[13] In addition, Wang and coworkers disclosed the Mn-catalyzed 1,6-conjugate addition/aromatization of *para*-quinone methides with dialkyl phosphonates and diaryl phosphine oxides, but the stoichiometric ratio of P(O)-H compounds to *p*-QMs is higher to 1.5:1 in this protocol.[14] Very recently, the base-catalyzed (Cs_2CO_3, DBU, *t*-BuONa) direct hydrophosphorylation of *para*-quinone methides with P(O)-H compounds were archived by Li, Wang, Jiang and our research groups.[15] Different to previous works, Pawar *et al*. discovered a green protocol for the synthesis of diaryl methyl-substituted phosphine oxides through the reaction of *p*-QMs with diaryl phosphine oxides in water (**Scheme 2**).[16] Although there are a number of studies on the direct phosphorylation of *p*-quinone methides with P(O)-H compounds, the use of simple P(III)-nucleophiles as starting materials are rare. The Michaelis-Arbuzov-type reactions of phosphites with 4-ethylidene-2,6-di-*tert*-butyl-2,5-cyclohexadiene-1-one, 2,6-di-*tert*-butyl-4-cyanomethylidene-2,5-cyclohexadien-1-one and fuchsone were investigated by Markovskii, Kolesnikov, Kopel'tsiv and their coworkers in the 1980s. However, these reactions were usually performed at a very high temperature. From the analysis of the nature of the chemical reaction, it can be seen that in the absence of a catalyst, this type of reaction is a typical thermodynamically controlled reaction in organic synthesis.[17] Encouraged by these elegant works, herein we disclosed a simple and efficient method for the silver-catalyzed regioselective phosphorylation of *p*-QMs with P(III) nucleophiles and water via the Michaelis-Arbuzov-type reaction.

Results and discussion

At the first stage of our study, we attempted to use AgOAc as the catalyst for the construction of P-C(sp^3) bond to synthesize diarylmethyl-substituted organophosphorus compounds. The reaction of 4-benzylidene-2,6-di-*tert*-butylcyclohexa-2,5-dienone (**1a**) with triethyl phosphite (**2a**) was performed at 80 ^oC in CH_2Cl_2 under air atmosphere with the addition of AgOAc (10 mol%), the corresponding phosphorylation product of diethyl ((3,5-di-*tert*-butyl-4-hydroxyphenyl)(phenyl)methyl)phosphonate (**3a**) was generated in 76% yield after the reaction (**Table 1**, entry 1). Some other silver salts such as AgOTf, $AgNO_3$, $AgBF_4$ and Ag_2CO_3 were screened as the catalyst for the reaction, and the results showed that $AgBF_4$ is the best (**Table 1**, entries 2-5). Besides CH_2Cl_2, some other solvents such as THF, 1,4-dioxane, toluene, DMF, CH_3CN and DCE (1,2-dichloroethane) were further investigated (**Table 1**, entry 4 and entries 6-11), the target product of **3a** is generated in a preferable yield of 97% in DCE. We then selected DCE as the solvent for further optimization. On the other hand, the amount of $AgBF_4$ used has a significant influence on the reaction. With the decrease of the use of $AgBF_4$ from 10 mol% to 1 mol%, the yield of the product was decreased sharply. When we increased the amount of $AgBF_4$ to 20 mol%, there was no further improvement for the yield of **3a** (**Table 1**, entry 9 and entries 12-16). In addition, when the reaction was conducted at room temperature, **3a** was only generated in 28% yield. With the increase of the reaction temperature, the yield of the target product was increased gradually, but by further increasing the temperature from 80 ^{o}C to 100 ^{o}C, there are no obvious effects on the reaction (**Table 1**, entry 9 and entries 17-20). Moreover, it should be noted that when the reaction was performed without the addition of water, there was no product detected during the reaction. Thus, this result proved that water is the crucial reactant for the reaction, but the excessive water could result in the hydrolysis of P(III)-nucleophiles during the reaction (**Table 1**, entry 9 and entries 21-23). Thus, the optimized reaction conditions are as follows: DCE (1.0 mL), $AgBF_4$ (10 mol%), H_2O (2.0 eq), air, 80 ^{o}C, 12 h.

Table 1. Optimization of the reaction conditions. [a]



Entry	Solvent	Catalyst	Temp.	Yield [b]
1	CH_2Cl_2	AgOAc	80 ^{o}C	76%
2	CH_2Cl_2	AgOTf	80 ^{o}C	67%
3	CH_2Cl_2	$AgNO_3$	80 ^{o}C	58%
4	CH_2Cl_2	$AgBF_4$	80 ^{o}C	89%
5	CH_2Cl_2	Ag_2CO_3	80 ^{o}C	56%
6	THF	$AgBF_4$	80 ^{o}C	87%
7	1,4-Dioxane	$AgBF_4$	80 ^{o}C	75%
8	Toluene	$AgBF_4$	80 ^{o}C	82%
9	**DCE**	**$AgBF_4$**	**80 ^{o}C**	**97%**
10	DMF	$AgBF_4$	80 ^{o}C	85%
11	CH_3CN	$AgBF_4$	80 ^{o}C	83%
12	DCE	-	80 ^{o}C	N.D.
13	DCE	$AgBF_4$	80 ^{o}C	58% [c]
14	DCE	$AgBF_4$	80 ^{o}C	67% [d]
15	DCE	$AgBF_4$	80 ^{o}C	76% [e]
16	DCE	$AgBF_4$	80 ^{o}C	96% [f]

17	DCE	AgBF$_4$	R.T.	28%
18	DCE	AgBF$_4$	40 °C	41%
19	DCE	AgBF$_4$	60 °C	70%
20	DCE	AgBF$_4$	100 °C	96%
21	DCE	AgBF$_4$	80 °C	N.D.[g]
22	DCE	AgBF$_4$	80 °C	79%[h]
23	DCE	AgBF$_4$	80 °C	92%[i]

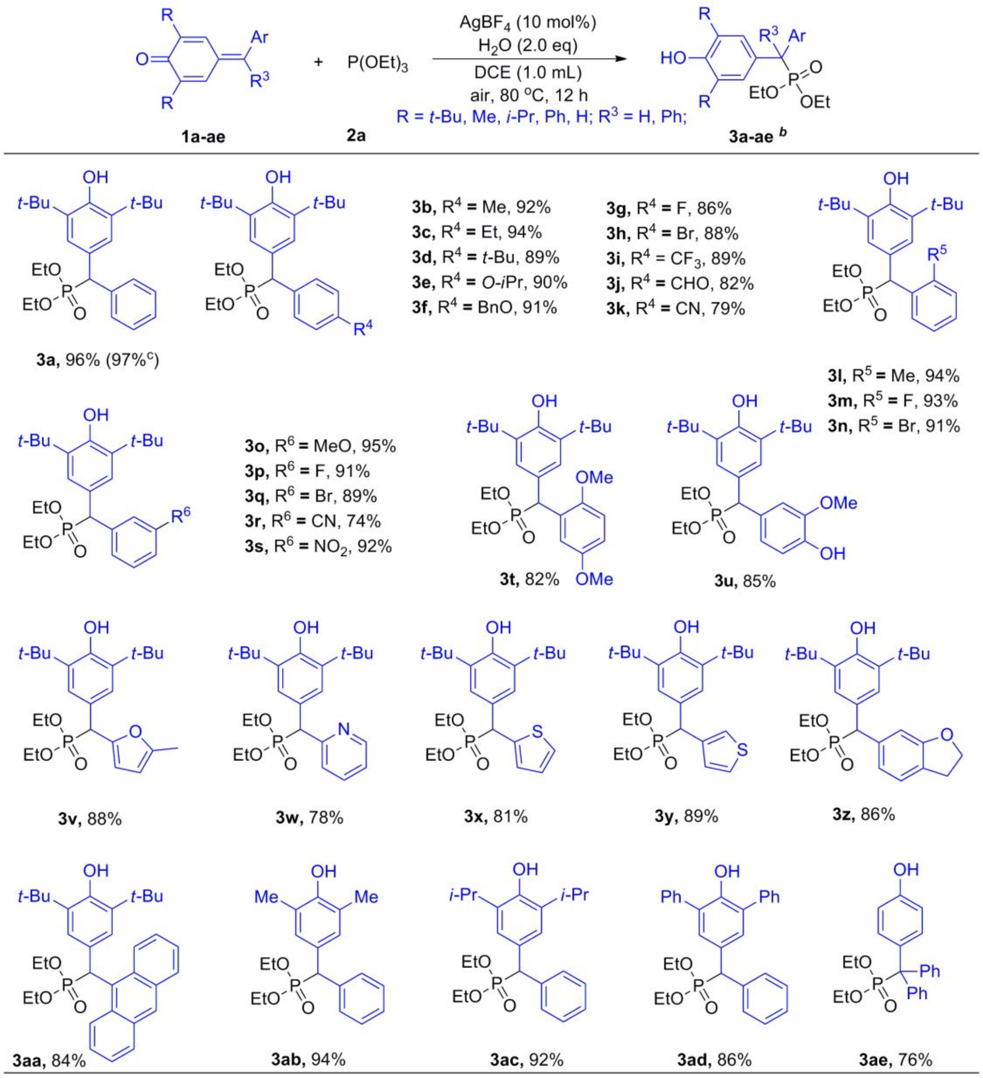
[a] Reactions were operated with triethyl phosphite (0.2 mmol), *para*-quinone methides (0.2 mmol), catalyst (10 mol%), H$_2$O (2.0 eq) and solvent (1.0 mL) under air stmosphere. [b] Yield determined by GC analysis, using dodecane as the internal standard, N.D. = not detected. [c] AgBF$_4$ (1 mol%). [d] AgBF$_4$ (2 mol%). [e] AgBF$_4$ (5 mol%). [f] AgBF$_4$ (20 mol%). [g] H$_2$O (0 eq). [h] H$_2$O (1.0 eq). [i] H$_2$O (3.0 eq).

As shown in **Scheme 3**, the silver-catalyzed regioselective phosphorylation of 4-benzylidene-2,6-di-*tert*-butylcyclohexa-2,5-dienone (**1a**) with triethyl phosphite (**2a**) leading to diethyl ((3,5-di-*tert*-butyl-4-hydroxyphenyl)(phenyl)methyl)phosphonate can be applied to different kinds of *para*-quinone methides (*p*-QMs). It is clear that the aryl moiety in *p*-QMs containing a *para*-electron donating groups, such as 4-CH$_3$ (**1b**), 4-Et (**1c**), 4-*t*-Bu (**1d**), 4-O-*i*-Pr (**1e**) and 4-OBn (**1f**), these compounds can react efficiently with triethyl phosphite (**2a**) under the optimized reaction conditions, affording the corresponding phosphorylation products of **3b**-**3f** in 89-94% yields. In addition, when 2,6-di-*tert*-butyl-4-(4-fluorobenzylidene)cyclohexa-2,5-dienone (**1g**), 4-(4-bromobenzylidene)-2,6-di-*tert*-butylcyclohexa-2,5-dienone (**1h**), 2,6-di-*tert*-butyl-4-(4-(trifluoromethyl)benzylidene) cyclohexa-2,5-dienone (**1i**), 4-((3,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)methyl)benzaldehyde (**1j**) and 4-((3,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)methyl)benzonitrile (**1k**) were employed as the substrates for the reaction, the desired phosphorylation products were obtained in 79-89% yields. It is worth noting that diethyl ((3,5-di-*tert*-butyl-4-hydroxyphenyl)(*o*-tolyl)methyl)phosphonate (**3l**), diethyl ((3,5-di-*tert*-butyl-4-hydroxyphenyl)(2-fluorophenyl)methyl)phosphonate (**3m**) and diethyl ((2-bromophenyl)(3,5-di-*tert*-butyl-4-hydroxyphenyl)methyl) phosphonate (**3n**) could be synthesized in 91-94% yields through the reactions of **1l**, **1m** and **1n** with triethyl phosphite (**2a**) under the present reaction conditions, although these compounds have a certain steric hindrance in the aryl ring. Furthermore, various kinds of *p*-QMs containing the electron-donating or electron-withdrawing groups (e.g., methoxy, fluoro, bromo, cynao and nitro, **1o**-**1s**) on the meta-aryl moiety also exhibit high reactivities toward the phosphorylation process, affording the corresponding products of **3o**-**3s** in 74-95% yields. Interestingly, **3t** and **3u** could be synthesized through the reactions of 2,6-di-*tert*-butyl-4-(2,5-dimethoxybenzylidene)cyclohexa-2,5-dienone (**1t**) and 2,6-di-*tert*-butyl-4-(4-hydroxy-3-methoxybenzylidene) cyclohexa-2,5-dienone (**1u**) with triethyl phosphite (**2a**) in 82% and 85% yields. To our surprise, a variety of heterocyclic *p*-QMs compounds (**1v**-**1z**) showed positive results for the reaction, affording the corresponding target products in 78-89% yields. Furthermore, diethyl (anthracen-9-yl(3,5-di-*tert*-butyl-4-hydroxyphenyl)methyl)phosphonate (**3aa**) can also be generated in 84% yield via the reaction of 4-(anthracen-9-ylmethylene)-2,6-di-*tert*-butylcyclohexa-2,5-dienone (**1aa**) with triethyl phosphite (**2a**). Notably, special *p*-QMs such as 4-benzylidene-2,6-dimethylcyclohexa-2,5-dienone (**1ab**), 4-benzylidene-2,6-diisopropylcyclohexa-2,5-dienone (**1ac**), 5'-benzylidene-[1,1':3',1''-terphenyl]-2'(5'H)-one (**1ad**) and 4-(diphenylmethylene)cyclohexa-2,5-dienone (**1ae**) were also found to be suitable for this transformation, and the target products of **3ab**-**3ae** could be generated in 76-94% yields as we expected.

As depicted in **Scheme 4**, it is clear that both trimethyl phosphite (**2b**) and tripropyl phosphite (**2c**) exhibit high reactivities toward **1a**, affording the expected phosphorylation products of **4a** and **4b** in 92% and 93% yields. Additionally, despite the bulky alkyl steric hindrance, some special phosphites such as triisopropyl phosphite (**2d**) and tributyl phosphite (**2e**) were well tolerated for the reaction, giving the expected phosphorylation products of **4c** and **4d** in 89% and 92% yields. In addition, tribenzyl phosphite (**2f**), tris(2,2,2-trifluoroethyl) phosphite (**2g**) and tris(1,1,1,3,3,3-hexafluoropropan-2-yl) phosphite (**2h**) were proved to be suitable nucleophiles for the reaction, producing the expected products of **4e**-**4g** in 81-87% yields. When methoxydiphenylphosphine (**2i**), ethoxydiphenylphosphine (**2j**) and iso-propoxydiphenylphosphine (**2k**) were employed as the nucleophiles, the corresponding product of ((3,5-di-*tert*-butyl-4-hydroxyphenyl)(phenyl)methyl) diphenylphos-phine oxide (**4h**) is generated in the range of 78-88% yields. In the case of *tert*-butoxydiphenylphosphine (**2l**), we have not detected the target product after the reaction, plausibly due to the fact of steric hindrance. Delightfully, different kinds of ethoxydiarylphosphine such as ethoxydi-*p*-tolylphosphine (**2m**), ethoxybis(4-

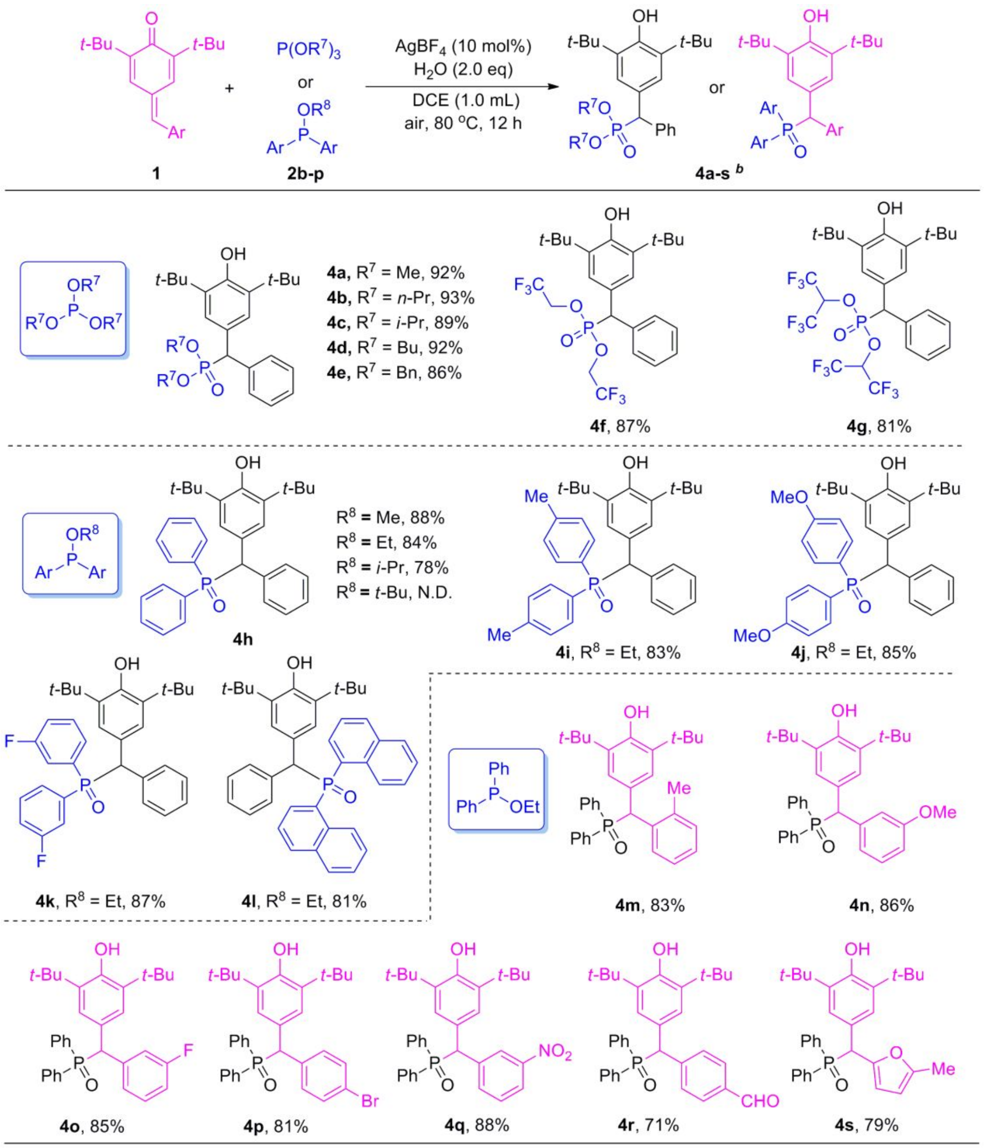
methoxyphenyl)phosphine (**2n**), ethoxybis(3-fluorophenyl)phosphine (**2o**) and ethoxydi(naphthalen-1-yl)phosphine (**2p**) also showed positive results for this transformation, affording the expected phosphorylation products of **4i**-**4l** in good yields.

Scheme 3. Substrate scope of *p*-QMs. [a]



[a] Reaction conditions: triethyl phosphite (0.2 mmol), *p*-QMs compounds (0.2 mmol), AgBF$_4$ (10 mol%), H$_2$O (2.0 eq), DCE (1.0 mL), air, 80 °C, 12 h. [b] Isolated yields. [c] GC yield.

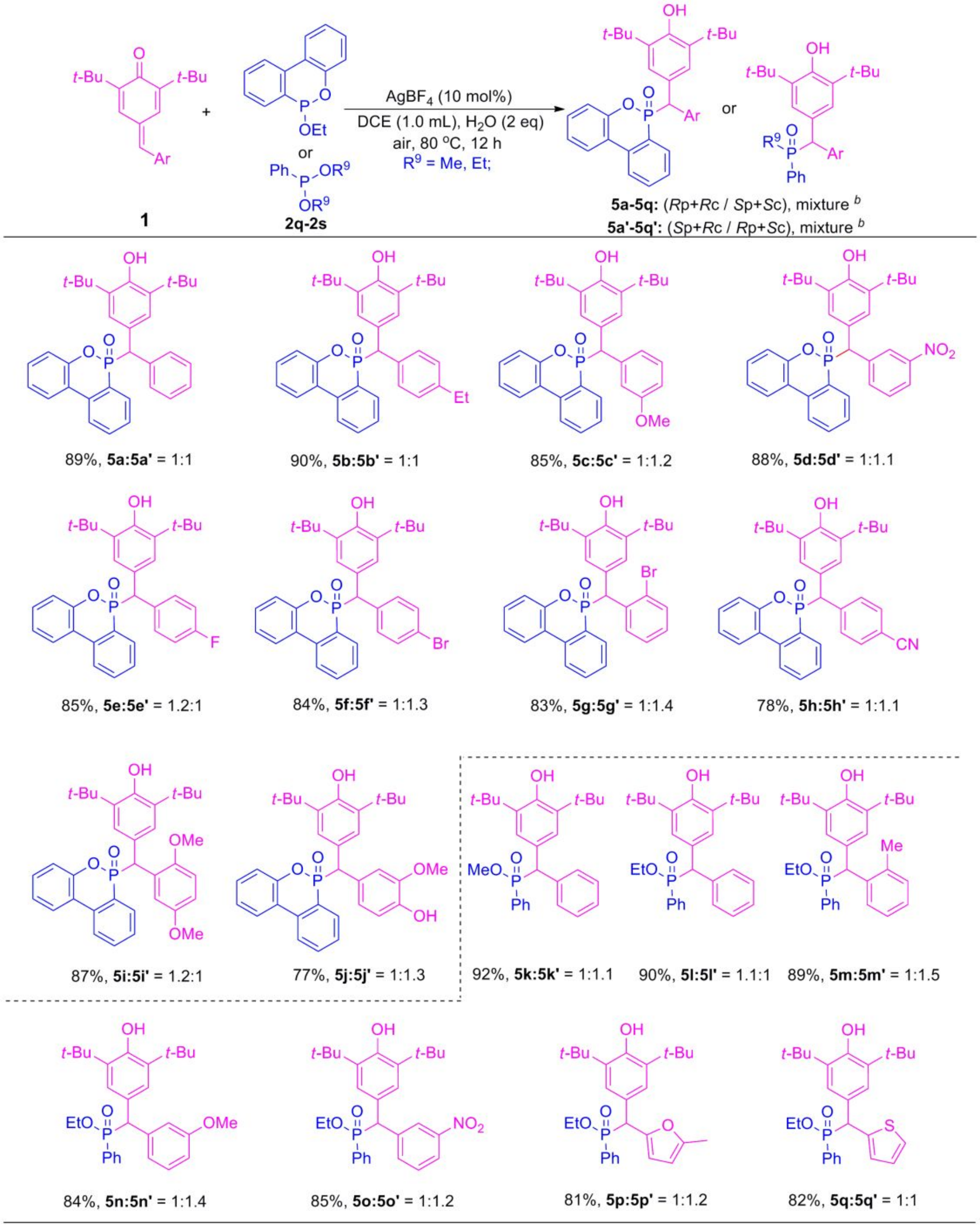
Scheme 4. Substrate scope of P(III)-nucleophiles.[a]



[a] Reaction conditions: *p*-QMs compounds, (0.2 mmol), P(III)-nucleophiles (0.2 mmol), $AgBF_4$ (10 mol%), H_2O (2.0 eq), DCE (1.0 mL), air, 80 °C, 12 h. [b] Isolated yields.

It is worth noting that when 2,6-di-*tert*-butyl-4-(2-methylbenzylidene)cyclohexa-2,5-dienone (**1l**), 2,6-di-*tert*-butyl-4-(3-methoxybenzylidene)cyclohexa-2,5-dienone (**1o**), 2,6-di-*tert*-butyl-4-(3-fluorobenzylidene)cyclohexa-2,5-dienone (**1p**), 4-(4-bromobenzylidene)-2,6-di-*tert*-butylcyclohexa-2,5-dienone (**1h**), 2,6-di-*tert*-butyl-4-(3-nitrobenzylidene)cyclohexa-2,5-dienone (**1s**), 4-((3,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)methyl) benzaldehyde (**1j**), and 2,6-di-*tert*-butyl-4-((5-methylfuran-2-yl)methylene)cyclohexa-2,5-dienone (**1v**) were employed, ethoxydiphenylphosphine (**2j**) could react efficiently with these compounds, the corresponding phosphorylation products of **4m**-**4s** could be isolated in 71-88% yields.

Scheme 5. Synthesis of (*R*p+*R*c/*S*p+*S*c)- and (*S*p+*R*c/*R*p+*S*c)- products.[b]



[a] Reaction conditions: *p*-QMs compounds, (0.2 mmol), P(III)-nucleophiles (0.2 mmol), AgBF$_4$ (10 mol%), H$_2$O (2.0 eq), DCE (1.0 mL), air, 80 °C, 12 h. [b] Isolated yields, the diastereoselectivity was calculated by ^{31}P-NMR analysis.

To our surprise, when 6-ethoxy-6H-dibenzo[c,e][1,2]oxaphosphinine (**2q**) was employed as the nucleophiles for this transformation, the corresponding enantiomers of **5a** (*R*p+*R*c/*S*p+*S*c) and **5a**'

(*S*p+*R*c/*R*p+*S*c) could be generated in 89 % yields with the ratio of 1:1. The configurations of compounds **5a** and **5a**' were confirmed unambiguously by X-ray single crystal analysis (**Figures 1** and **2**). As illustrated in **Scheme 5**, different kinds of *p*-QMs compounds, such as 2,6-di-*tert*-butyl-4-(4-ethylbenzylidene)cyclohexa-2,5-dienone (**1c**), 2,6-di-*tert*-butyl-4-(3-methoxybenzylidene)cyclohexa-2,5-dienone (**1o**), 2,6-di-*tert*-butyl-4-(3-nitrobenzylidene)cyclohexa-2,5-dienone (**1s**), 2,6-di-*tert*-butyl-4-(4-fluorobenzylidene)cyclohexa-2,5-dienone (**1g**), 4-(4-bromobenzylidene)-2,6-di-*tert*-butylcyclohexa-2,5-dienone (**1h**), 4-(2-bromobenzylidene)-2,6-di-*tert*-butylcyclohexa-2,5-dienone (**1n**), 4-((3,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)methyl) benzonitrile (**1k**), 2,6-di-*tert*-butyl-4-(2,5-dimethoxybenzylidene) cyclohexa-2,5-dienone (**1t**) and 2,6-di-*tert*-butyl-4-(4-hydroxy-3-methoxybenzylidene)cyclohexa-2,5-dienone (**1u**) can react efficiently with **2q** to afford the corresponding enantiomers in 77-90% yields. In addition, it is observed that dimethyl phenylphosphonite (**2r**) and diethyl phenylphosphonite (**2s**) also have the high reactivity toward the reaction, yielding the expected enantiomers with 92% and 90% yields (**5k**:**5k**' = 1:1.1; **5l**:**5l**' = 1.1:1). Furthermore, when 2,6-di-*tert*-butyl-4-(2-methylbenzylidene)cyclohexa-2,5-dienone (**1l**), 2,6-di-*tert*-butyl-4-(3-methoxybenzylidene)cyclohexa-2,5-dienone (**1o**), 2,6-di-*tert*-butyl-4-(3-nitrobenzylidene)cyclohexa-2,5-dienone (**1s**), 2,6-di-*tert*-butyl-4-((5-methylfuran-2-yl)methylene)cyclohexa-2,5-dienone (**1v**) and 2,6-di-*tert*-butyl-4-(thiophen-2-ylmethylene)cyclohexa-2,5-dienone (**1x**) were used as substrates in the reaction to react with diethyl phenylphosphonite (**2r**), the enantiomers could be synthesized in 81-89% yields. In the above reactions, because of the reaction was performed without the assistance of chiral ligands, the diastereoselectivity for the enantiomers is mainly ascribed to the steric hindrance or the electronic effects of substituents in *p*-QMs.

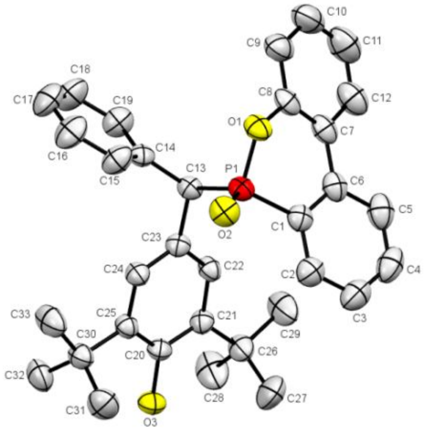


Figure 1. ORTEP drawing of compound **5a** (enantiomer: *R*p+*R*c/*S*p+*S*c).[18] Hydrogen atoms are omitted for clarity; ellipsoids are drawn at 50% probability.

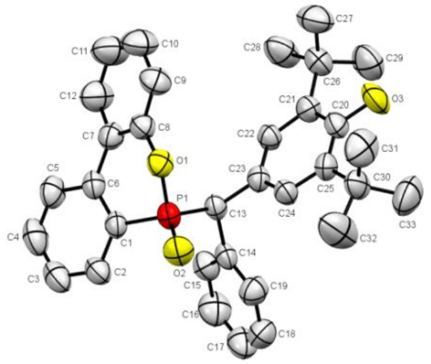
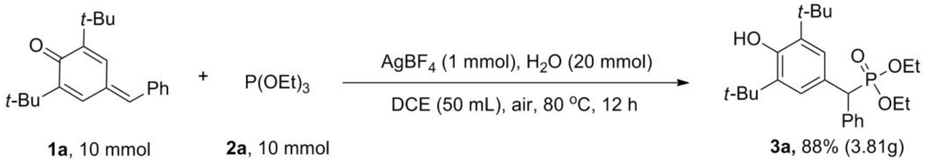


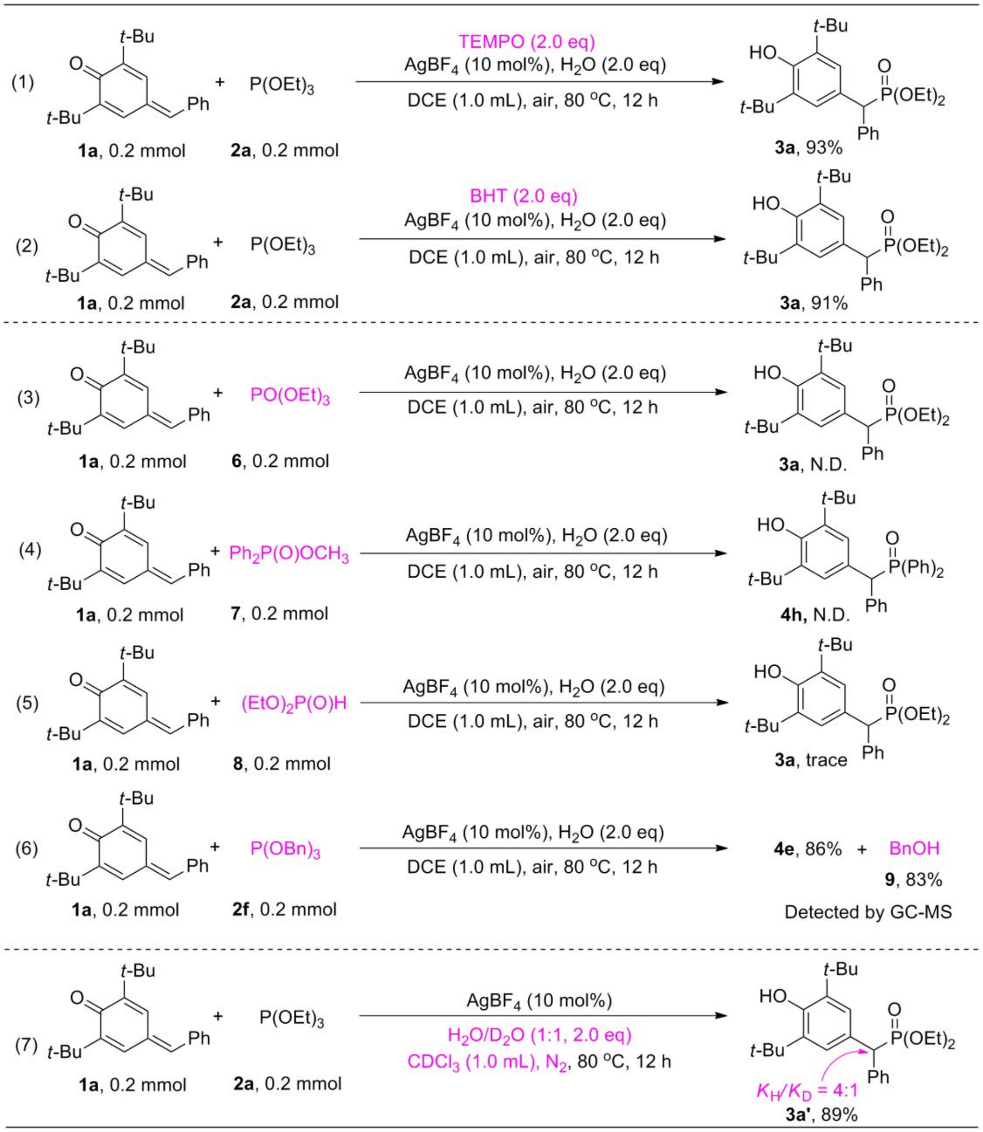
Figure 2. ORTEP drawing of compound **5a**' (enantiomer: *S*p+*R*c/*R*p+*S*c).[18] Hydrogen atoms and chloroform are omitted for clarity; ellipsoids are drawn at 50% probability.

Scheme 6. Large-Scale Synthesis of **3a**.



In order to demonstrate the practical application of this transformation, a large-scale reaction of 4-benzylidene-2,6-di-*tert*-butylcyclohexa-2,5-dienone (**1a**, 10 mmol) with triethylphosphite (**2a**, 10 mmol) were performed out at the optimized reaction conditions, and the target product of **3a** was obtained in 88% yield (3.81 g, **Scheme 6**).

Scheme 7. Control experiments.



As depicted in **Scheme 7**, a series of control experiments were carried out to gain the insight of the reaction. When the reaction was performed under the optimized reaction conditions with the addition of 2,2,6,6-tetramethylpiperidine *N*-oxyl (TEMPO) or 2,6-di-*tert*-butyl-4-methylphenolradical (BHT) as the radical scavenger, the phosphorylation product **3a** could be formed in 93% or 91% yield, respectively. These results indicated that the mechanism is not processed via a radical process (eqs 1 and 2). In addition, when triethyl phosphate and methyl diphenylphosphinate were used as nucleophiles for the reaction, as monitored by GC and GC-MS, the expected products were not detected during the reaction (eqs 3 and 4). Considering that triethyl phosphite is very easy to operate for the hydrolysis under the present conditions to give the corresponding diethyl phosphonate, we then adopted diethyl phosphonate as the phosphorylation reagent for the reaction. However, only a trace amount of **3a** was produced after the reaction (eqs 5). It is deduced that diethyl phosphonate is not the key intermediate for the reaction. In addition, when tribenzyl phosphite (**2f**) is used as the substrate under the optimized reaction conditions, as monitored by GC-MS, the corresponding benzyl alcohol (**9**) is generated as a by-product in 83% yield (eqs 6). Based on these results, we further performed a kinetic isotope effect (KIE) experiment between H_2O and D_2O for this reaction. A KIE (k_H/k_D) constant was determined as 4.0 (eqs 7). On the other hand, the corresponding ^{31}P NMR spectroscopy tracking experiments were conducted under the optimal reaction conditions. As shown in **Figure 3**, the ^{31}P signal of the possible intermediate of the reaction is captured at δ = 7.28. As the reaction time increases, the signal of the intermediate gradually disappears, and the raw material is gradually transformed into the target product.

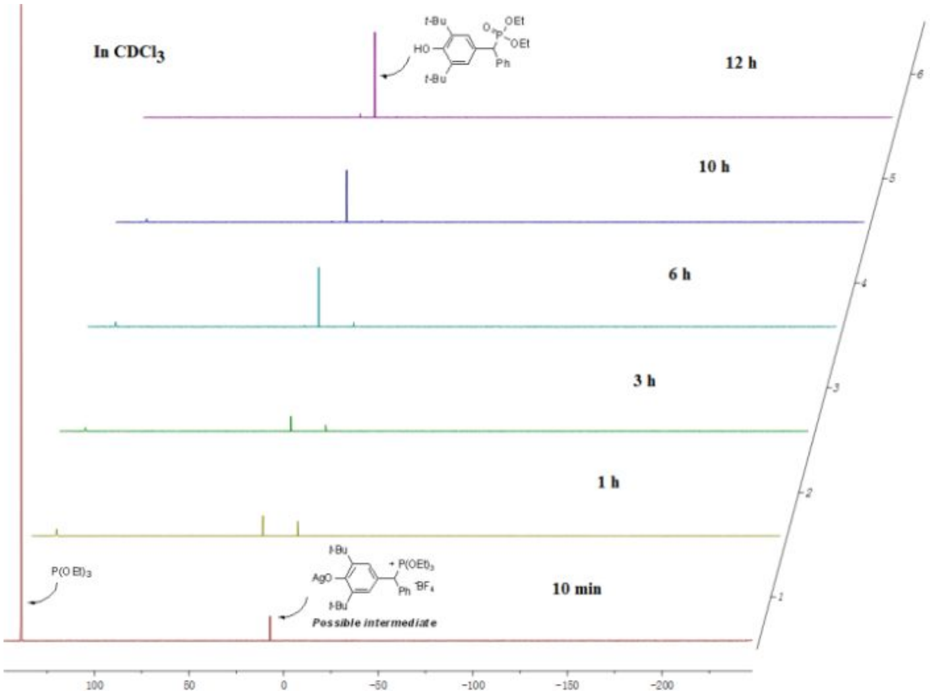
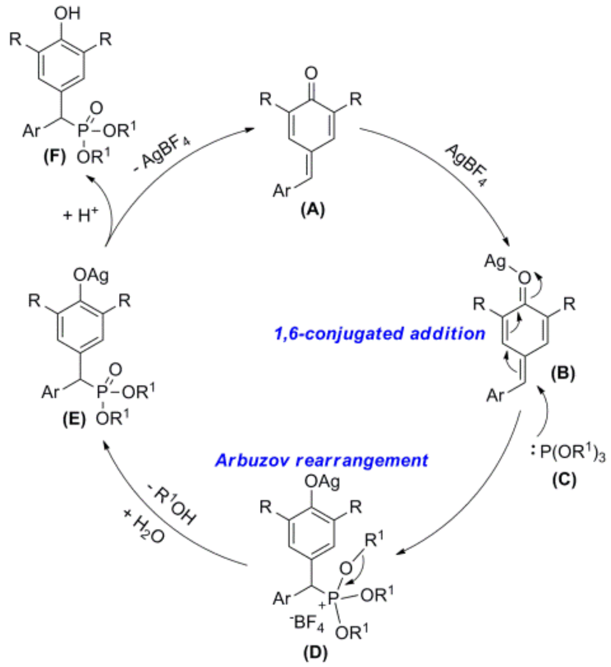


Figure 3. ^{31}P NMR tracking experiments.

Scheme 8. A plausible mechanism.



A plausible mechanism for the silver-catalyzed regioselective phosphorylation of *p*-QMs compounds with P(III)-nucleophiles is proposed in **Scheme 8**. Firstly, $AgBF_4$ initially activates the carbonyl group of *p*-QMs **(A)** to form the intermediate **B**. In the presence of a P(III)-nucleophile **(C)**, **B** could react with **C** efficiently via the 1,6-conjugated addition/aromatization processes to generate the possible intermediate **(D)**. With the assistance of H_2O, **E** was formed directly via the Michaelis-Arbuzov-type rearrangement from **D**. Finally, the target product **(F)** is generated through the hydrogen-atom transfer process, and the silver cation was regenerated and reused in the next catalytic cycle.

Conclusions

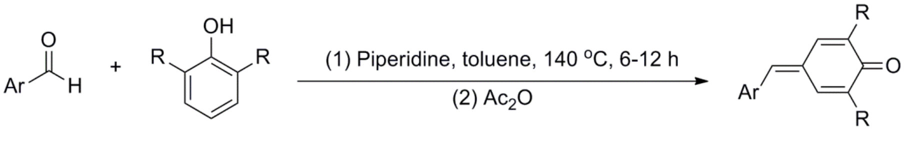
In summary, we developed an efficient method for the synthesis of α-diarylmethyl-substituted organophosphorus compounds through the silver catalyzed regioselective phosphorylation of *para*-quinone methides with P(III)-nucleophiles via the Michaelis-Arbuzov-type reaction. A wide range of P(III)-nucleophiles and *p*-QMs containing different functional groups were tolerated well for this transformation. To the best of our knowledge, the direct phosphorylation of *p*-QMs with P(III)-nucleophiles by silver catalysis has not been investigated previously. The possible mechanism was studied by step-by-step control experiments and ^{31}P NMR tracking experiments. This synthetic method also has high potential for the construction of pharmacology active α-diarylmethyl substituted organophosphorus compounds.

Experimental Section

General Considerations:

All solvents used in the reactions were freshly distilled. The other reagents were recrystallized or distilled as necessary. All reactions were performed under an atmosphere of air unless specified otherwise. ^{1}H (400 MHz), ^{13}C (100 MHz), ^{31}P (160 MHz), ^{19}F (376 MHz) were recorded on a 400 MHz spectrometer in $CDCl_3$. ^{1}H NMR chemical shifts were reported using TMS as the internal standard while ^{13}C NMR chemical shifts were reported relative to $CDCl_3$. The electron ionization method was used for HRMS measurements, and the mass analyzer type was double-focusing.

General Procedure for the Preparation of *p*-Quinone Methides (*p*-QMs). According to the reported procedure,[9f] 2,6-di-*tert*-butylphenol (20 mmol) and 1.0 equiv of aldehyde (20 mmol) were dissolved in toluene (0.25 M) and the mixture was heated to 140 °C in a Dean-Stark apparatus (oil bath). Piperidine (2.0 equiv, 40 mmol) was added dropwise over 1 h, and the reaction mixture was refluxed for 6-12 h. After cooling just below the boiling point of the mixture, acetic anhydride (2.0 equiv, 40 mmol) was added and stirring was continued for 15 min. Then the reaction mixture was poured into ice-water, extracted with DCM, and dried over Na_2SO_4, the solvent was evaporated, and the residue was dried in vacuo. Pure *p*-QMs product was obtained by passing the crude product through a short silica gel column using *n*-hexane as eluent. Some other substituents (e.g., -Cl, -OMe) in substituted *p*-QMs failed to give the isolated products in the reactions of 2,6-dimethoxyphenol and 2,6-dichlorophenol with benzaldehyde.



General procedure. A mixture of *para*-quinone methides (*p*-QMs) (0.2 mmol), P(III)-nucleophiles (1.0 eq, 0.20 mmol), $AgBF_4$ (0.1 eq, 0.02 mmol) and H_2O (2.0 eq, 0.4 mmol) were dissolved in DCE (1.0 mL) under an air atmosphere stirred for 12.0 h at 80 ^oC. Upon completion of the reaction, the mixture was concentrated under vacuum. Removal of the solvent under a reduced pressure gave the crude product; pure product was obtained by passing the crude product through a short silica gel column using hexane/EtOAc (10:1-1:1) as eluent.

Synthesis of P(III)-nucleophiles. A mixture of PCl_3 or $RPCl_2$ or R_2PCl (10 mmol), alcohol (for PCl_3, 3.3 equiv, 33 mmol; for $RPCl_2$, 2.2 equiv, 22 mmol; for R_2PCl, 1.1 equiv, 11 mmol;), pyridine (for PCl_3, 3.3 equiv, 33 mmol; for $RPCl_2$, 2.2 equiv, 22 mmol; for R_2PCl, 1.1 equiv, 11 mmol;) were dissolved in THF (10 mL) under a N_2 atmosphere stirred for 12.0 h at room temperature. Upon completion of the reaction, the mixture was concentrated under vacuum. Removal of the solvent under a reduced pressure gave the crude product; pure product was obtained by passing the crude product through a short silica gel column using hexane/EtOAc (10:1-1:1) as eluent.

*Diethyl ((3,5-di-tert-butyl-4-hydroxyphenyl)(phenyl)methyl)phosphonate (**3a**).* According to the general procedure, work-up and flash column chromatography (R_f = 0.4, Hexane/EtOAc: 5:1) gave product **3a** (82.1 mg, 0.19 mmol, 96%) as a colorless oil,[15b] ^1H NMR (400 MHz, $CDCl_3$, 25 ^oC, TMS): δ = 7.45-7.47 (m, 2H), 7.21-7.25 (m, 4H), 7.13-7.18 (m, 1H), 5.07 (s, 1H), 4.26 (d, J = 25.4 Hz, 1H), 3.82-3.92 (m, 2H), 3.67-3.79 (m, 2H), 1.34 (s, 18H), 1.01 (dt, J = 11.6, 7.1 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 ^oC, TMS): δ = 152.9 (d, J(C,P) = 2.5 Hz), 137.4 (d, J(C,P) = 4.8 Hz), 135.8 (d, J(C,P) = 1.5 Hz), 129.5 (d, J(C,P) = 8.0 Hz), 128.5 (d, J(C,P) = 1.2 Hz), 127.0 (d, J(C,P) = 21.6 Hz), 126.9 (d, J(C,P) = 8.8 Hz), 126.2 (d, J(C,P) = 7.9 Hz), 62.5 (dd, ^1J(C,P) = 17.7 Hz, ^2J(C,P) = 7.1 Hz), 51.2 (d, J(C,P) = 136.8 Hz), 34.4 (s), 30.3 (s), 16.2 (t, J(C,P) = 5.9 Hz); $^{31}P\{^1H\}$ NMR (160 MHz, $CDCl_3$, 25 ^oC, TMS): δ = 25.9.

*Diethyl ((3,5-di-tert-butyl-4-hydroxyphenyl)(p-tolyl)methyl)phosphonate (**3b**).* According to the general procedure, work-up and flash column chromatography (R_f = 0.5, hexane/EtOAc: 2:1) gave product **3b** (80.4 mg, 0.18 mmol, 92%) as a colorless oil.[15a] ^1H NMR (400 MHz, $CDCl_3$, 25 ^oC, TMS): δ = 7.41-7.43 (m, 2H), 7.30-7.31 (m, 2H), 7.11-7.13 (m, 2H), 5.12 (s, 1H), 4.29 (d, J = 25.3 Hz, 1H), 3.89-4.00 (m, 2H), 3.74-3.87 (m, 2H), 2.31 (s, 3H), 1.41 (s, 18H), 1.09 (dt, *J* = 19.3, 7.1 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 152.9 (d, *J*(C,P) = 2.5 Hz), 136.5 (d, *J*(C,P) = 2.3 Hz), 135.7 (d, *J*(C,P) = 1.5 Hz), 134.4 (d, *J*(C,P) = 4.9 Hz), 129.3 (d, *J*(C,P) = 8.0 Hz), 129.2 (d, *J*(C,P) = 1.3 Hz), 127.3 (d, *J*(C,P) = 5.4 Hz), 126.1 (d, *J*(C,P) = 7.9 Hz), 62.5 (dd, ^1J(C,P) = 19.0 Hz, ^2J(C,P) = 7.1 Hz), 50.8 (d, *J*(C,P) = 136.8 Hz), 34.4 (s), 30.3 (s), 21.1 (s), 16.3 (dd, ^1J(C,P) = 9.3 Hz, ^2J(C,P) = 5.9 Hz); $^{31}P\{^1H\}$ NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 26.1.

*Diethyl ((3,5-di-tert-butyl-4-hydroxyphenyl)(4-ethylphenyl)methyl)phosphonate (**3c**).* According to the general procedure, work-up and flash column chromatography (R_f = 0.5, hexane/EtOAc: 2:1) gave product **3c** (87.4 mg, 0.19 mmol, 94%) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.43-7.46 (m, 2H), 7.31-7.32 (m, 2H), 7.13-7.15 (m, 2H), 5.13 (s, 1H), 4.30 (d, *J* = 25.4 Hz, 1H), 3.73-4.00 (m, 4H), 2.58-2.64 (m, 2H), 1.41 (s, 18H), 1.20 (t, *J* = 7.6 Hz, 3H), 1.09 (dt, *J* = 19.3, 7.1 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 152.9 (d, *J*(C,P) = 2.5 Hz), 142.8 (d, *J*(C,P) = 2.4 Hz), 135.8 (d, *J*(C,P) = 1.5 Hz), 134.5 (d, *J*(C,P) = 4.9 Hz), 129.3 (d, *J*(C,P) = 7.9 Hz), 128.0 (d, *J*(C,P) = 1.3 Hz), 127.3 (d, *J*(C,P) = 5.4 Hz), 126.2 (d, *J*(C,P) = 7.9 Hz), 62.5 (dd, ^1J(C,P) = 22.4 Hz, ^2J(C,P) = 7.1 Hz), 50.8 (d, *J*(C,P) = 136.6 Hz), 34.4 (s), 30.3 (s), 28.4 (s), 16.3 (dd, ^1J(C,P) = 8.2 Hz, ^2J(C,P) = 5.9 Hz), 15.52 (s); $^{31}P\{^1H\}$ NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 26.2. HRMS (ESI) *m*/*z*: calcd. for $C_{27}H_{42}O_4P$ $[M+H]^+$: 461.2821, found: 461.2815.

*Diethyl ((4-(tert-butyl)phenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)phosphonate (**3d**).* According to the general procedure, work-up and flash column chromatography (R_f = 0.4, hexane/EtOAc: 2:1) gave product **3d** (86.9 mg, 0.18 mmol, 89%) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.44-7.46 (m, 2H), 7.31-7.33 (m, 4H), 5.12 (s, 1H), 4.30 (d, *J* = 25.4 Hz, 1H), 3.72-4.00 (m, 4H), 1.42 (s, 18H), 1.29 (s, 9H), 1.08 (dt, *J* = 23.0, 7.1 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 152.9 (d, *J*(C,P) = 2.5 Hz), 150.0 (d, *J*(C,P) = 2.5 Hz), 135.7 (d, *J*(C,P) = 1.5 Hz), 134.2 (d, *J*(C,P) = 5.0 Hz), 128.9 (d, *J*(C,P) = 7.8 Hz), 127.2 (d, *J*(C,P) = 5.4 Hz), 126.2 (d, *J*(C,P) = 8.0 Hz), 125.4 (d, *J*(C,P) = 1.5 Hz), 62.5 (dd, ^1J(C,P) = 30.9 Hz, ^2J(C,P) = 7.1 Hz), 50.8 (d, *J*(C,P) = 136.4 Hz), 34.4 (s), 31.3 (s), 30.3 (s), 16.2 (t, *J*(C,P) = 6.3 Hz), 15.52 (s); $^{31}P\{^1H\}$ NMR (160

MHz, $CDCl_3$, 25 °C, TMS): δ = 26.2. HRMS (ESI) *m/z*: calcd. for $C_{29}H_{46}O_4P$ $[M+H]^+$: 489.3134, found: 489.3129.

*Diethyl ((3,5-di-tert-butyl-4-hydroxyphenyl)(4-isopropoxyphenyl)methyl)phosphonate **(3e)**.* According to the general procedure, work-up and flash column chromatography (R_f = 0.5, hexane/EtOAc: 5:1) gave product **3e** (88.3 mg, 0.18 mmol, 90%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.42-7.44 (m, 2H), 7.29-7.30 (m, 2H), 6.82-7.85 (m, 2H), 5.14 (s, 1H), 4.47-4.56 (m, 1H), 4.27 (d, *J* = 25.5 Hz, 1H), 3.73-4.00 (m, 4H), 1.41 (s, 18H), 1.31 (d, *J* = 6.1 Hz, 6H), 1.09 (dt, *J* = 16.6, 7.1 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 156.8 (d, *J*(C,P) = 2.1 Hz), 152.8 (d, *J*(C,P) = 2.4 Hz), 135.8 (d, *J*(C,P) = 1.5 Hz), 130.5 (d, *J*(C,P) = 8.0 Hz), 129.2 (d, *J*(C,P) = 5.1 Hz), 127.4 (d, *J*(C,P) = 5.1 Hz), 126.1 (d, *J*(C,P) = 7.8 Hz), 115.9 (d, *J*(C,P) = 1.0 Hz), 69.8 (s), 62.5 (dd, ^1J(C,P) = 10.5 Hz, ^2J(C,P) = 7.1 Hz), 50.2 (d, *J*(C,P) = 137.0 Hz), 34.4 (s), 30.3 (s), 22.1 (d, *J*(C,P) = 1.6 Hz), 16.3 (dd, ^1J(C,P) = 9.3 Hz, ^2J(C,P) = 5.8 Hz); $^{31}P\{^1H\}$ NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 26.2. HRMS (ESI) *m/z*: calcd. for $C_{28}H_{44}O_5P$ $[M+H]^+$: 491.2926, found: 491.2921.

*Diethyl ((4-(benzyloxy)phenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)phosphonate **(3f)**.* According to the general procedure, work-up and flash column chromatography (R_f = 0.5, hexane/EtOAc: 2:1) gave product **3f** (98.1 mg, 0.18 mmol, 91%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.25-7.46 (m, 9H), 6.92-6.94 (m, 2H), 5.12 (s, 1H), 5.04 (s, 2H), 4.28 (d, *J* = 25.5 Hz, 1H), 3.74-3.99 (m, 4H), 1.41 (s, 18H), 1.09 (dt, *J* = 15.9, 7.1 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 157.8 (d, *J*(C,P) = 2.1 Hz), 152.9 (d, *J*(C,P) = 2.6 Hz), 137.03 (s), 135.7 (d, *J*(C,P) = 1.5 Hz), 130.5 (d, *J*(C,P) = 8.0 Hz), 129.7 (d, *J*(C,P) = 5.1 Hz), 128.6 (s), 127.9 (s), 127.5 (s), 127.3 (d, *J*(C,P) = 5.1 Hz), 126.1 (d, *J*(C,P) = 7.7 Hz), 114.9 (d, *J*(C,P) = 1.1 Hz), 70.0 (s), 62.5 (dd, ^1J(C,P) = 13.9 Hz, ^2J(C,P) = 7.1 Hz), 50.2 (d, *J*(C,P) = 136.9), 34.4 (s), 30.3 (s), 16.3 (dd, ^1J(C,P) = 10.1 Hz, ^2J(C,P) = 5.8 Hz); $^{31}P\{^1H\}$ NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 26.2. HRMS (ESI) *m/z*: calcd. for $C_{32}H_{42}O_5P$ $[M-H]^-$: 537.2770, found: 537.2767.

*Diethyl ((3,5-di-tert-butyl-4-hydroxyphenyl)(4-fluorophenyl)methyl)phosphonate **(3g)**.* According to the general procedure, work-up and flash column chromatography (R_f = 0.5, hexane/EtOAc: 2:1) gave product **3g** (76.5 mg, 0.17 mmol, 86%) as a colorless oil.[15a] ^{1}H NMR (400 MHz, CDCl$_3$, 25 ^{o}C, TMS): δ = 7.49-7.53 (m, 2H), 7.27-7.28 (m, 2H), 6.98-7.03 (m, 2H), 5.17 (s, 1H), 4.32 (d, *J* = 25.5 Hz, 1H), 3.74-4.01 (m, 4H), 1.41 (s, 18H), 1.10 (dt, *J* = 20.4, 7.1 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$, 25 ^{o}C, TMS): δ = 161.9 (dd, ^{1}*J*(C,F) = 244.0 Hz), ^{2}*J*(C,P) = 2.1 Hz), 153.0 (d, *J*(C,P) = 2.5 Hz), 135.9 (d, *J*(C,P) = 1.5 Hz), 133.2 (dd, ^{1}*J*(C,F) = 4.8 Hz), ^{2}*J*(C,P) = 3.4 Hz), 131.0 (t, *J*(C,F) = 8.0 Hz), 126.8 (d, *J*(C,P) = 5.4 Hz), 126.1 (d, *J*(C,P) = 7.8 Hz), 115.3 (dd, ^{1}*J*(C,F) = 21.1 Hz), ^{2}*J*(C,P) = 1.3 Hz), 62.6 (dd, ^{1}*J*(C,P) = 29.5 Hz, ^{2}*J*(C,P) = 7.2 Hz), 50.2 (d, *J*(C,P) = 137.5 Hz), 34.4 (s), 30.3 (s), 16.2 (dd, ^{1}*J*(C,P) = 8.8 Hz, ^{2}*J*(C,P) = 5.8 Hz); ^{31}P{^{1}H} NMR (160 MHz, CDCl$_3$, 25 ^{o}C, TMS): δ = 25.6 (d, *J*(P,F) = 3.5 Hz); ^{19}F{^{1}H} NMR (376 MHz, CDCl$_3$, 25 ^{o}C, TMS): δ = -116. 0 (d, *J*(F,P) = 3.6 Hz).

*Diethyl ((4-bromophenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)phosphonate (**3h**).* According to the general procedure, work-up and flash column chromatography (R$_f$ = 0.4, hexane/EtOAc: 2:1) gave product **3h** (89.7 mg, 0.17 mmol, 88%) as a colorless oil.[14] ^{1}H NMR (400 MHz, CDCl$_3$, 25 ^{o}C, TMS): δ = 7.40-7.45 (m, 4H), 7.26-7.27 (m, 2H), 5.16 (s, 1H), 4.28 (d, *J* = 25.3 Hz, 1H), 3.73-4.02 (m, 4H), 1.41 (s, 18H), 1.09 (dt, *J* = 28.5, 7.1 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$, 25 ^{o}C, TMS): δ = 153.1 (d, *J*(C,P) = 2.4 Hz), 136.6 (d, *J*(C,P) = 4.8 Hz), 136.0 (d, *J*(C,P) = 1.4 Hz), 131.6 (d, *J*(C,P) = 1.2 Hz), 131.1 (d, *J*(C,P) = 8.0 Hz), 126.5 (d, *J*(C,P) = 5.4 Hz), 126.1 (d, *J*(C,P) = 7.8 Hz), 121.0 (d, *J*(C,P) = 2.9 Hz), 62.7 (dd, ^{1}*J*(C,P) = 37.4 Hz, ^{2}*J*(C,P) = 7.1 Hz), 50.5 (d, *J*(C,P) = 137.5 Hz), 34.4 (s), 30.3 (s), 16.3 (dd, ^{1}*J*(C,P) = 11.3 Hz, ^{2}*J*(C,P) = 5.9 Hz); ^{31}P{^{1}H} NMR (160 MHz, CDCl$_3$, 25 ^{o}C, TMS): δ = 25.2.

*Diethyl ((3,5-di-tert-butyl-4-hydroxyphenyl)(4-(trifluoromethyl)phenyl)methyl)phosphonate (**3i**).* According to the general procedure, work-up and flash column chromatography (R$_f$ = 0.5, hexane/EtOAc: 2:1) gave product **3i** (89.1 mg, 0.18 mmol, 89%) as a yellow oil. ^{1}H NMR (400 MHz, CDCl$_3$, 25 ^{o}C, TMS): δ = 7.65-7.67 (m, 2H), 7.56-7.58 (m, 2H), 7.29-7.30 (m, 2H), 5.18 (s, 1H), 4.38 (d, *J* = 25.3 Hz, 1H), 3.73-4.35 (m, 4H), 1.42 (s, 18H), 1.10 (dt, *J* = 31.2, 7.1 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$, 25 ^{o}C, TMS): δ = 153.2 (d, *J*(C,P) = 2.4 Hz), 141.7 (d, *J*(C,P) = 4.6 Hz), 136.1 (d, *J*(C,P) = 1.4 Hz), 129.7 (d, *J*(C,P) = 7.8 Hz), 129.1 (dd, ^{1}*J*(C,F) = 321.0 Hz), ^{2}*J*(C,P) = 2.1 Hz), 126.2 (d, *J*(C,P) = 7.9 Hz), 126.1 (s), 125.4 (d, *J*(C,F) = 1.3 Hz), 125.3 (d, *J*(C,F) = 1.1 Hz), 62.7 (dd, ^{1}*J*(C,P) = 55.9 Hz, ^{2}*J*(C,P) = 7.0 Hz), 50.9 (d, *J*(C,P) = 137.5 Hz), 34.4 (s), 30.3 (s), 16.2 (dd, ^{1}*J*(C,P) = 9.6 Hz,

^{2}J(C,P) = 5.8 Hz); ^{31}P{^{1}H} NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 24.9; ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$, 25 °C, TMS): δ = -62.5 (d, J(F,P) = 1.5 Hz). HRMS (ESI) *m*/*z*: calcd. for $C_{26}H_{37}F_3O_4P$ $[M+H]^+$: 501.2382, found: 501.2374.

*Diethyl ((3,5-di-tert-butyl-4-hydroxyphenyl)(4-formylphenyl)methyl)phosphonate (**3j**)*. According to the general procedure, work-up and flash column chromatography (R_f = 0.5, hexane/EtOAc: 1:1) gave product **3j** (75.5 mg, 0.16 mmol, 82%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 9.99 (s, 1H), 7.83-7.85 (m, 2H), 7.71-7.73 (m, 2H), 7.30-7.31 (m, 2H), 5.20 (s, 1H), 4.42 (d, J = 25.3 Hz, 1H), 3.75-4.03 (m, 4H), 1.42 (s, 18H), 1.10 (dt, J = 23.8, 7.1 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 192.0 (s), 153.2 (d, J(C,P) = 2.4 Hz), 144.7 (d, J(C,P) = 4.7 Hz), 136.1 (d, J(C,P) = 1.4 Hz), 135.1 (d, J(C,P) = 2.1 Hz), 130.1 (d, J(C,P) = 7.8 Hz), 129.9 (d, J(C,P) = 0.9 Hz), 126.2 (d, J(C,P) = 7.8 Hz), 126.0 (d, J(C,P) = 5.8 Hz), 62.8 (dd, ^{1}J(C,P) = 51.1 Hz, ^{2}J(C,P) = 7.0 Hz), 51.3 (d, J(C,P) = 137.3 Hz), 34.4 (s), 30.3 (s), 16.2 (dd, ^{1}J(C,P) = 8.9 Hz, ^{2}J(C,P) = 5.8 Hz); ^{31}P{^{1}H} NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 24.6. HRMS (ESI) *m*/*z*: calcd. for $C_{26}H_{38}O_5P$ $[M+H]^+$: 461.2457, found: 461.2454.

*Diethyl ((4-cyanophenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)phosphonate (**3k**)*. According to the general procedure, work-up and flash column chromatography (R_f = 0.4, hexane/EtOAc: 2:1) gave product **3k** (73.1 mg, 0.16 mmol, 79%) as a colorless oil.[15a] ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.60-7.67 (m, 4H), 7.26-7.27 (m, 2H), 5.20 (s, 1H), 4.37 (d, J = 25.3 Hz, 1H), 3.73-4.03 (m, 4H), 1.41 (s, 18H), 1.10 (dt, J = 34.4, 7.0 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 153.3 (d, J(C,P) = 2.4 Hz), 143.2 (d, J(C,P) = 4.6 Hz), 136.2 (d, J(C,P) = 1.4 Hz), 132.2 (d, J(C,P) = 1.3 Hz), 130.2 (d, J(C,P) = 7.8 Hz), 126.1 (d, J(C,P) = 7.9 Hz), 125.7 (d, J(C,P) = 5.8 Hz), 118.9 (s), 110.8 (d, J(C,P) = 2.4 Hz), 62.8 (dd, ^{1}J(C,P) = 67.3 Hz, ^{2}J(C,P) = 7.0 Hz), 51.1 (d, J(C,P) = 137.7 Hz), 34.4 (s), 30.3 (s), 16.2 (dd, ^{1}J(C,P) = 11.1 Hz, ^{2}J(C,P) = 5.8 Hz); ^{31}P{^{1}H} NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 24.3.

*Diethyl ((3,5-di-tert-butyl-4-hydroxyphenyl)(o-tolyl)methyl)phosphonate (**3l**)*. According to the general procedure, work-up and flash column chromatography (R_f = 0.5, hexane/EtOAc: 2:1) gave product **3l** (83.8 mg, 0.19 mmol, 94%) as a colorless oil.[15a] ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C, TMS): δ = 7.85-7.87 (m, 1H), 7.20-7.21 (m, 2H), 7.11-7.17 (m, 1H), 7.03-7.08 (m, 2H), 5.04 (s, 1H), 4.51 (d, *J* = 26.1 Hz, 1H), 3.67-3.90 (m, 4H), 2.30 (s, 3H), 1.32 (s, 18H), 1.10 (dt, *J* = 7.1, 1.5 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$, 25 °C, TMS): δ = 152.8 (d, *J*(C,P) = 2.7 Hz), 136.2 (d, *J*(C,P) = 11.7 Hz), 135.9 (d, *J*(C,P) = 3.5 Hz), 135.6 (d, *J*(C,P) = 1.7 Hz), 130.5 (s), 129.3 (d, *J*(C,P) = 5.3 Hz), 126.8 (d, *J*(C,P) = 1.6 Hz), 126.6 (d, *J*(C,P) = 5.7 Hz), 126.4 (d, *J*(C,P) = 7.6 Hz), 126.2 (d, *J*(C,P) = 1.7 Hz), 62.5 (t, *J*(C,P) = 6.6 Hz), 46.2 (d, *J*(C,P) = 138.0 Hz), 34.4 (s), 30.3 (s), 20.24 (s), 16.3 (dd, ^{1}*J*(C,P) = 5.8 Hz, ^{2}*J*(C,P) = 1.3 Hz); ^{31}P{^{1}H} NMR (160 MHz, CDCl$_3$, 25 °C, TMS): δ = 26.9.

*Diethyl ((3,5-di-tert-butyl-4-hydroxyphenyl)(2-fluorophenyl)methyl)phosphonate (**3m**).* According to the general procedure, work-up and flash column chromatography (R_f = 0.3, hexane/EtOAc: 2:1) gave product **3m** (83.7 mg, 0.19 mmol, 93%) as a colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C, TMS): δ = 7.91-7.95 (m, 1H), 7.33-7.34 (m, 2H), 7.12-7.24 (m, 2H), 7.00-7.04 (m, 1H), 5.16 (s, 1H), 4.79 (d, *J* = 25.3 Hz, 1H), 3.77-4.03 (m, 4H), 1.41 (s, 18H), 1.10 (dt, *J* = 19.3, 7.1 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$, 25 °C, TMS): δ = 160.3 (dd, ^{1}*J*(C,F) = 244.0 Hz, ^{2}*J*(C,P) = 10.4 Hz), 153.0 (d, *J*(C,P) = 2.5 Hz), 135.9 (d, *J*(C,P) = 1.5 Hz), 130.7 (dd, ^{1}*J*(C,F) = 5.1 Hz, ^{2}*J*(C,P) = 2.8 Hz), 128.5 (d, *J*(C,P) = 10.3 Hz), 126.3 (d, *J*(C,P) = 7.6 Hz), 126.2 (d, *J*(C,P) = 5.4 Hz), 124.9 (dd, ^{1}*J*(C,F) = 14.6 Hz, ^{2}*J*(C,P) = 3.6 Hz), 124.1 (dd, ^{1}*J*(C,F) = 3.5 Hz, ^{2}*J*(C,P) = 2.2 Hz), 115.3 (d, *J*(C,F) = 22.8 Hz), 62.6 (dd, ^{1}*J*(C,P) = 36.5 Hz, ^{2}*J*(C,P) = 7.0 Hz), 41.5 (dd, ^{1}*J*(C,P) = 140.2 Hz, ^{2}*J*(C,F) = 3.3 Hz), 34.4 (s), 30.3 (s), 16.2 (dd, ^{1}*J*(C,P) = 7.2 Hz, ^{2}*J*(C,P) = 6.0 Hz); ^{31}P{^{1}H} NMR (160 MHz, CDCl$_3$, 25 °C, TMS): δ = 25.4 (d, *J*(P,F) = 4.4 Hz); ^{19}F{^{1}H} NMR (376 MHz, CDCl$_3$, 25 °C, TMS): δ = -118.0 (d, *J*(F,P) = 4.4 Hz). HRMS (ESI) *m*/*z*: calcd. for $C_{25}H_{37}FO_4P$ [M+H]$^+$: 451.2413, found: 451.2408.

*Diethyl ((2-bromophenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)phosphonate (**3n**).* According to the general procedure, work-up and flash column chromatography (R_f = 0.5, hexane/EtOAc: 2:1) gave product **3n** (92.8 mg, 0.18 mmol, 91%) as a colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C, TMS): δ = 8.07-8.10 (m, 1H), 7.53-7.56 (m, 1H), 7.30-7.38 (m, 3H), 7.05-7.10 (m, 1H), 5.14 (s, 1H), 5.03 (d, *J* = 25.5 Hz, 1H), 3.77-4.02 (m, 4H), 1.41 (s, 18H), 1.10 (dt, *J* = 19.3, 7.1 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$, 25 °C, TMS): δ = 153.0 (d, *J*(C,P) = 2.5 Hz), 137.3 (d, *J*(C,P) = 1.9 Hz), 135.8 (d, *J*(C,P)

= 1.4 Hz), 133.00 (s), 130.8 (d, *J*(C,P) = 5.1 Hz), 128.4 (d, *J*(C,P) = 1.7 Hz), 127.7 (d, *J*(C,P) = 1.8 Hz), 126.4 (d, *J*(C,P) = 7.9 Hz), 126.2 (d, *J*(C,P) = 5.3 Hz), 125.4 (d, *J*(C,P) = 13.3 Hz), 62.6 (dd, ^1J(C,P) = 37.0 Hz, ^2J(C,P) = 6.6 Hz), 48.7 (d, *J*(C,P) = 139.6 Hz), 34.4 (s), 30.3 (s), 16.2 (dd, ^1J(C,P) = 7.1 Hz, ^2J(C,P) = 5.9 Hz); ^{31}P{^{1}H} NMR (160 MHz, CDCl$_3$, 25 ^{o}C, TMS): δ = 25.5. HRMS (ESI) *m*/*z*: calcd. for $C_{25}H_{37}BrO_4P$ [M+H]$^+$: 511.1613, found: 511.1609.

*Diethyl ((3,5-di-tert-butyl-4-hydroxyphenyl)(3-methoxyphenyl)methyl)phosphonate (**3o**).* According to the general procedure, work-up and flash column chromatography (R_f = 0.4, hexane/EtOAc: 2:1) gave product **3o** (87.8 mg, 0.19 mmol, 95%) as a colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$, 25 ^{o}C, TMS): δ = 7.32-7.33 (m, 2H), 7.21-7.25 (m, 1H), 7.11-7.15 (m, 2H), 6.77-6.79 (m, 1H), 5.14 (s, 1H), 4.30 (d, *J* = 25.3 Hz, 1H), 3.74-4.02 (m, 7H), 1.41 (s, 18H), 1.10 (dt, *J* = 23.0, 7.1 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$, 25 ^{o}C, TMS): δ = 159.5 (d, *J*(C,P) = 1.0 Hz), 152.9 (d, *J*(C,P) = 2.5 Hz), 138.8 (d, *J*(C,P) = 4.7 Hz), 135.8 (d, *J*(C,P) = 1.5 Hz), 129.4 (s), 126.9 (d, *J*(C,P) = 5.6 Hz), 126.2 (d, *J*(C,P) = 7.8 Hz), 121.9 (d, *J*(C,P) = 7.9 Hz), 115.0 (d, *J*(C,P) = 8.2 Hz), 112.6 (d, *J*(C,P) = 2.2 Hz), 62.5 (dd, ^1J(C,P) = 19.7 Hz, ^2J(C,P) = 7.1 Hz), 55.2 (s), 51.1 (d, *J*(C,P) = 136.7 Hz), 34.4 (s), 30.3 (s), 16.3 (dd, ^1J(C,P) = 9.6 Hz, ^2J(C,P) = 5.9 Hz); ^{31}P{^{1}H} NMR (160 MHz, CDCl$_3$, 25 ^{o}C, TMS): δ = 25.8. HRMS (ESI) *m*/*z*: calcd. for $C_{26}H_{38}O_5P$ [M-H]$^-$: 461.2457, found: 461.2451.

*Diethyl ((3,5-di-tert-butyl-4-hydroxyphenyl)(3-fluorophenyl)methyl)phosphonate (**3p**).* According to the general procedure, work-up and flash column chromatography (R_f = 0.5, hexane/EtOAc: 2:1) gave product **3p** (81.9 mg, 0.18 mmol, 91%) as a colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$, 25 ^{o}C, TMS): δ = 7.24-7.34 (m, 5H), 6.91-6.95 (m, 1H), 5.18 (s, 1H), 4.32 (d, *J* = 25.3 Hz, 1H), 3.74-4.03 (m, 4H), 1.42 (s, 18H), 1.10 (dt, *J* = 29.9, 7.1 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$, 25 ^{o}C, TMS): δ = 162.7 (dd, ^1J(C,F) = 244.0 Hz, ^2J(C,P) = 1.1 Hz), 153.1 (d, *J*(C,P) = 2.5 Hz), 139.9 (dd, ^1J(C,F) = 7.3 Hz, ^2J(C,P) = 4.7 Hz), 136.0 (d, *J*(C,P) = 1.4 Hz), 129.8 (dd, ^1J(C,F) = 8.3 Hz, ^2J(C,P) = 1.4 Hz), 126.4 (d, *J*(C,P) = 5.7 Hz), 126.2 (d, *J*(C,P) = 7.9 Hz), 125.2 (dd, ^1J(C,F) = 7.9 Hz, ^2J(C,P) = 2.8 Hz), 116.5 (dd, ^1J(C,F) = 22.2 Hz, ^2J(C,P) = 8.0 Hz), 113.9 (dd, ^1J(C,F) = 21.0 Hz, ^2J(C,P) = 2.1 Hz), 62.7 (dd, ^1J(C,P) = 36.8 Hz, ^2J(C,P) = 7.0 Hz), 50.8 (dd, ^1J(C,P) = 137.4 Hz, ^2J(C,F) = 1.5 Hz), 34.4 (s), 30.3 (s), 16.2 (dd, ^1J(C,P) = 9.9 Hz, ^2J(C,P) = 5.8 Hz); ^{31}P{^{1}H} NMR (160 MHz, CDCl$_3$, 25 ^{o}C, TMS): δ = 25.1 (s); ^{19}F{^{1}H} NMR

(376 MHz, $CDCl_3$, 25 °C, TMS): δ = -112.9 (s). HRMS (ESI) *m/z*: calcd. for $C_{25}H_{37}FO_4P$ $[M+H]^+$: 451.2413, found: 451.2409.

*Diethyl ((3-bromophenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)phosphonate (**3q**).* According to the general procedure, work-up and flash column chromatography (R_f = 0.4, hexane/EtOAc: 2:1) gave product **3q** (90.8 mg, 0.18 mmol, 89%) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.62-7.65 (m, 1H), 7.53-7.54 (m, 1H), 7.36-7.38 (m, 1H), 7.27-7.28 (m, 2H), 7.17-7.21 (m, 1H), 5.17 (s, 1H), 4.28 (d, *J* = 25.3 Hz, 1H), 3.73-4.03 (m, 4H), 1.42 (s, 18H), 1.11 (dt, *J* = 31.5, 7.1 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 153.1 (d, *J*(C,P) = 2.5 Hz), 139.8 (d, *J*(C,P) = 4.7 Hz), 136.0 (d, *J*(C,P) = 1.5 Hz), 132.6 (d, *J*(C,P) = 8.8 Hz), 130.0 (d, *J*(C,P) = 2.2 Hz), 129.9 (d, *J*(C,P) = 1.6 Hz), 128.0 (d, *J*(C,P) = 7.2 Hz), 126.3 (d, *J*(C,P) = 5.8 Hz), 126.2 (d, *J*(C,P) = 7.7 Hz), 122.4 (d, *J*(C,P) = 0.9 Hz), 62.7 (dd, ^1J(C,P) = 35.8 Hz, ^2J(C,P) = 7.1 Hz), 50.9 (d, *J*(C,P) = 137.5 Hz), 34.4 (s), 30.3 (s), 16.3 (dd, ^1J(C,P) = 10.3 Hz, ^2J(C,P) = 5.8 Hz); $^{31}P\{^1H\}$ NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 25.0. HRMS (ESI) *m/z*: calcd. for $C_{25}H_{37}BrO_4P$ $[M+H]^+$: 511.1613, found: 511.1605.

*Diethyl ((3-cyanophenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)phosphonate (**3r**).* According to the general procedure, work-up and flash column chromatography (R_f = 0.5, hexane/EtOAc: 2:1) gave product **3r** (67.6 mg, 0.15 mmol, 74%) as a colorless oil.[15a] ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.77-7.84 (m, 2H), 7.53-7.55 (m, 1H), 7.41-7.45 (m, 1H), 7.27-7.28 (m, 2H), 5.23 (s, 1H), 4.35 (d, *J* = 25.4 Hz, 1H), 3.73-4.04 (m, 4H), 1.42 (s, 18H), 1.11 (dt, *J* = 38.7, 7.1 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 153.3 (d, *J*(C,P) = 2.3 Hz), 139.3 (d, *J*(C,P) = 4.6 Hz), 136.3 (d, *J*(C,P) = 1.3 Hz), 133.9 (d, *J*(C,P) = 7.3 Hz), 130.0 (d, *J*(C,P) = 8.5 Hz), 130.6 (d, *J*(C,P) = 2.1 Hz), 129.3 (d, *J*(C,P) = 1.3 Hz), 126.1 (d, *J*(C,P) = 7.9 Hz), 125.7 (d, *J*(C,P) = 5.5 Hz), 118.84 (s), 112.5 (d, *J*(C,P) = 1.0 Hz), 62.8 (dd, ^1J(C,P) = 68.9 Hz, ^2J(C,P) = 7.0 Hz), 50.6 (d, *J*(C,P) = 138.0 Hz), 34.4 (s), 30.3 (s), 16.2 (dd, ^1J(C,P) = 12.8 Hz, ^2J(C,P) = 5.8 Hz); $^{31}P\{^1H\}$ NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 24.4.

*Diethyl ((3,5-di-tert-butyl-4-hydroxyphenyl)(3-nitrophenyl)methyl)phosphonate (**3s**).* According to the general procedure, work-up and flash column chromatography (R_f = 0.5, hexane/EtOAc: 2:1) gave product **3s** (87.8 mg, 0.18 mmol, 92%) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ =

8.35-8.36 (m, 1H), 8.10-8.12 (m, 1H), 7.94-7.96 (m, 1H), 7.48-7.52 (m, 1H), 7.30-7.31 (m, 2H), 5.21 (s, 1H), 4.43 (d, *J* = 25.4 Hz, 1H), 3.75-4.05 (m, 4H), 1.42 (s, 18H), 1.12 (dt, *J* = 41.2, 7.1 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 153.4 (d, *J*(C,P) = 2.4 Hz), 148.22 (s), 139.8 (d, *J*(C,P) = 4.7 Hz), 136.3 (d, *J*(C,P) = 1.4 Hz), 135.4 (d, *J*(C,P) = 6.8 Hz), 129.4 (d, *J*(C,P) = 1.5 Hz), 126.2 (d, *J*(C,P) = 7.9 Hz), 125.6 (d, *J*(C,P) = 5.6 Hz), 124.5 (d, *J*(C,P) = 8.7 Hz), 122.0 (d, *J*(C,P) = 2.1 Hz), 62.8 (dd, ^1J(C,P) = 75.5 Hz, ^2J(C,P) = 7.1 Hz), 50.7 (d, *J*(C,P) = 137.8 Hz), 34.4 (s), 30.3 (s), 16.2 (dd, ^1J(C,P) = 12.9 Hz, ^2J(C,P) = 5.8 Hz); $^{31}P\{^1H\}$ NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 24.3. HRMS (ESI) *m*/*z*: calcd. for $C_{25}H_{37}NO_6P$ $[M+H]^+$: 478.2358, found: 478.2350.

*Diethyl ((3,5-di-tert-butyl-4-hydroxyphenyl)(2,5-dimethoxyphenyl)methyl)phosphonate (**3t**).* According to the general procedure, work-up and flash column chromatography (R_f = 0.4, hexane/EtOAc: 2:1) gave product **3t** (80.7 mg, 0.16 mmol, 82%) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.54-7.55 (m, 1H), 7.36-7.37 (m, 2H), 6.72-6.80 (m, 2H), 5.10 (s, 1H), 5.03 (d, *J* = 25.2 Hz, 1H), 3.77-4.03 (m, 10H), 1.41 (s, 18H), 1.11 (dt, *J* = 19.8, 7.1 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 153.5 (d, *J*(C,P) = 2.2 Hz), 152.8 (d, *J*(C,P) = 2.6 Hz), 151.0 (d, *J*(C,P) = 10.1 Hz), 135.5 (d, *J*(C,P) = 1.6 Hz), 127.1 (d, *J*(C,P) = 3.9 Hz), 127.0 (s), 126.4 (d, *J*(C,P) = 7.8 Hz), 115.6 (d, *J*(C,P) = 5.2 Hz), 113.4 (d, *J*(C,P) = 2.0 Hz), 112.0 (s), 62.4 (dd, ^1J(C,P) = 17.3 Hz, ^2J(C,P) = 7.0 Hz), 56.54 (s), 55.71 (s), 41.3 (d, *J*(C,P) = 139.3 Hz), 34.4 (s), 30.3 (s), 16.3 (dd, ^1J(C,P) = 8.9 Hz, ^2J(C,P) = 5.8 Hz); $^{31}P\{^1H\}$ NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 26.8. HRMS (ESI) *m*/*z*: calcd. for $C_{27}H_{42}O_6P$ $[M+H]^+$: 493.2719, found: 493.2715.

*Diethyl ((3,5-di-tert-butyl-4-hydroxyphenyl)(4-hydroxy-3-methoxyphenyl)methyl)phosphonate (**3u**).* According to the general procedure, work-up and flash column chromatography (R_f = 0.5, hexane/EtOAc: 2:1) gave product **3u** (81.3 mg, 0.17 mmol, 85%) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.30-7.31 (m, 2H), 7.16-7.17 (m, 1H), 6.95-6.98 (m, 1H), 6.83-6.85 (m, 1H), 5.91 (s, 1H), 5.13 (s, 1H), 4.26 (d, *J* = 25.5 Hz, 1H), 3.74-4.01 (m, 7H), 1.41 (s, 18H), 1.10 (dt, *J* = 18.9, 7.1 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 152.9 (d, *J*(C,P) = 2.6 Hz), 146.4 (d, *J*(C,P) = 1.4 Hz), 144.8 (d, *J*(C,P) = 2.3 Hz), 135.7 (d, *J*(C,P) = 1.6 Hz), 128.9 (d, *J*(C,P) = 4.9 Hz), 127.2 (d, *J*(C,P) = 5.3 Hz), 126.0 (d, *J*(C,P) = 7.7 Hz), 122.5 (d, *J*(C,P) = 9.1 Hz), 114.4 (d, *J*(C,P) = 1.2

Hz), 112.1 (d, *J*(C,P) = 7.4 Hz), 62.5 (dd, ^{1}J(C,P) = 11.1 Hz, ^{2}J(C,P) = 7.1 Hz), 55.8 (s), 50.5 (d, *J*(C,P) = 136.9 Hz), 34.4 (s), 30.3 (s), 16.3 (dd, ^{1}J(C,P) = 10.3 Hz, ^{2}J(C,P) = 5.9 Hz); ^{31}P{^{1}H} NMR (160 MHz, CDCl$_3$, 25 °C, TMS): δ = 26.1. HRMS (ESI) *m*/*z*: calcd. for $C_{26}H_{40}O_6P$ [M+H]$^+$: 479.2563, found: 479.2559.

*Diethyl ((3,5-di-tert-butyl-4-hydroxyphenyl)(5-methylfuran-2-yl)methyl)phosphonate (**3v**).* According to the general procedure, work-up and flash column chromatography (R$_f$ = 0.5, hexane/EtOAc: 2:1) gave product **3v** (76.7 mg, 0.18 mmol, 88%) as a yellow oil. ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C, TMS): δ = 7.23-7.24 (m, 2H), 6.33-6.35 (m, 1H), 5.91-5.92 (m, 1H), 5.14 (s, 1H), 4.39 (d, *J* = 26.1 Hz, 1H), 3.72-4.07 (m, 4H), 2.25 (s, 3H), 1.42 (s, 18H), 1.16 (dt, *J* = 46.4, 7.1 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$, 25 °C, TMS): δ = 153.1 (d, *J*(C,P) = 3.3 Hz), 151.3 (d, *J*(C,P) = 2.4 Hz), 148.4 (d, *J*(C,P) = 2.6 Hz), 135.7 (d, *J*(C,P) = 2.4 Hz), 126.1 (d, *J*(C,P) = 6.2 Hz), 124.9 (d, *J*(C,P) = 6.4 Hz), 109.2 (d, *J*(C,P) = 5.5 Hz), 106.6 (d, *J*(C,P) = 1.9 Hz), 62.7 (dd, ^{1}J(C,P) = 10.4 Hz, ^{2}J(C,P) = 7.0 Hz), 45.0 (d, *J*(C,P) = 139.4 Hz), 34.4 (s), 30.3 (s), 16.3 (dd, ^{1}J(C,P) = 15.9 Hz, ^{2}J(C,P) = 6.0 Hz), 13.60 (s); ^{31}P{^{1}H} NMR (160 MHz, CDCl$_3$, 25 °C, TMS): δ = 23.0. HRMS (ESI) *m*/*z*: calcd. for $C_{24}H_{36}O_5P$ [M-H]$^-$: 435.2300, found: 435.2294.

*Diethyl ((3,5-di-tert-butyl-4-hydroxyphenyl)(pyridin-2-yl)methyl)phosphonate (**3w**).* According to the general procedure, work-up and flash column chromatography (R$_f$ = 0.5, hexane/EtOAc: 1:1) gave product **3w** (67.5 mg, 0.16 mmol, 78%) as a colorless oil.[14] ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C, TMS): δ = 8.55-8.56 (m, 1H), 7.63-7.73 (m, 2H), 7.37-7.38 (m, 2H), 7.15-7.18 (m, 1H), 5.15 (s, 1H), 4.64 (d, *J* = 24.3 Hz, 1H), 3.84-4.04 (m, 4H), 1.41 (s, 18H), 1.12 (dt, *J* = 18.5, 7.1 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$, 25 °C, TMS): δ = 157.5 (d, *J*(C,P) = 2.6 Hz), 153.1 (d, *J*(C,P) = 2.8 Hz), 149.2 (s), 136.67 (s), 135.8 (d, *J*(C,P) = 1.8 Hz), 126.4 (s), 126.3 (s), 125.9 (d, *J*(C,P) = 6.4 Hz), 123.9 (d, *J*(C,P) = 4.9 Hz), 122.0 (d, *J*(C,P) = 1.5 Hz), 62.6 (dd, ^{1}J(C,P) = 51.6 Hz, ^{2}J(C,P) = 6.9 Hz), 53.9 (d, *J*(C,P) = 135.6 Hz), 34.4 (s), 30.3 (s), 16.3 (dd, ^{1}J(C,P) = 8.0 Hz, ^{2}J(C,P) = 6.0 Hz); ^{31}P{^{1}H} NMR (160 MHz, CDCl$_3$, 25 °C, TMS): δ = 24.7.

*Diethyl ((3,5-di-tert-butyl-4-hydroxyphenyl)(thiophen-2-yl)methyl)phosphonate (**3x**).* According to the general procedure, work-up and flash column chromatography (R$_f$ = 0.4, hexane/EtOAc: 2:1) gave product **3x** (71.1 mg, 0.16 mmol, 81%) as a yellow oil.[15a] ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.31-7.32 (m, 2H), 7.17-7.19 (m, 2H), 6.94-6.97 (m, 1H), 5.20 (s, 1H), 4.58 (d, *J* = 25.8 Hz, 1H), 3.69-4.09 (m, 4H), 1.42 (s, 18H), 1.12 (dt, *J* = 52.3, 7.1 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 153.2 (d, *J*(C,P) = 2.8 Hz), 139.6 (d, *J*(C,P) = 5.3 Hz), 135.8 (d, *J*(C,P) = 2.0 Hz), 126.8 (d, *J*(C,P) = 5.3 Hz), 126.7 (s), 126.5 (d, *J*(C,P) = 5.9 Hz), 126.1 (d, *J*(C,P) = 6.9 Hz), 124.7 (d, *J*(C,P) = 2.8 Hz), 62.9 (dd, ^{1}*J*(C,P) = 33.0 Hz, ^{2}*J*(C,P) = 7.0 Hz), 46.3 (d, *J*(C,P) = 139.4 Hz), 34.4 (s), 30.3 (s), 16.3 (dd, ^{1}*J*(C,P) = 17.1 Hz, ^{2}*J*(C,P) = 5.9 Hz); ^{31}P{^{1}H} NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 23.8.

*Diethyl ((3,5-di-tert-butyl-4-hydroxyphenyl)(thiophen-3-yl)methyl)phosphonate (**3y**).* According to the general procedure, work-up and flash column chromatography (R_f = 0.4, hexane/EtOAc: 2:1) gave product **3y** (78.1 mg, 0.18 mmol, 89%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.21-7.34 (m, 5H), 5.17 (s, 1H), 4.46 (d, *J* = 25.2 Hz, 1H), 3.69-4.03 (m, 4H), 1.41 (s, 18H), 1.11 (dt, *J* = 38.5, 7.1 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 153.0 (d, *J*(C,P) = 2.9 Hz), 137.0 (d, *J*(C,P) = 5.2 Hz), 135.8 (d, *J*(C,P) = 2.0 Hz), 129.0 (d, *J*(C,P) = 6.9 Hz), 126.5 (d, *J*(C,P) = 6.2 Hz), 126.1 (d, *J*(C,P) = 7.1 Hz), 125.3 (s), 123.2 (d, *J*(C,P) = 9.5 Hz), 62.6 (dd, ^{1}*J*(C,P) = 29.2 Hz, ^{2}*J*(C,P) = 7.0 Hz), 46.5 (d, *J*(C,P) = 138.1 Hz), 34.4 (s), 30.3 (s), 16.3 (dd, ^{1}*J*(C,P) = 13.5 Hz, ^{2}*J*(C,P) = 5.9 Hz); ^{31}P{^{1}H} NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 25.3. HRMS (ESI) *m*/*z*: calcd. for $C_{23}H_{34}O_4PS$ $[M-H]^-$: 437.1915, found: 437.1910.

*Diethyl ((3,5-di-tert-butyl-4-hydroxyphenyl)(2,3-dihydrobenzofuran-6-yl)methyl)phosphonate (**3z**).* According to the general procedure, work-up and flash column chromatography (R_f = 0.5, hexane/EtOAc: 2:1) gave product **3z** (81.5 mg, 0.17 mmol, 86%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.36-7.37 (m, 1H), 7.25-7.30 (m, 3H), 6.71-6.73 (m, 1H), 5.13 (s, 1H), 4.53 (t, *J* = 8.7 Hz, 2H), 4.26 (d, *J* = 25.5 Hz, 1H), 3.74-4.01 (m, 4H), 3.12-3.25 (m, 2H), 1.41 (s, 18H), 1.10 (dt, *J* = 24.9, 7.1 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 159.1 (d, *J*(C,P) = 2.1 Hz), 152.8 (d, *J*(C,P) = 2.4 Hz), 135.8 (d, *J*(C,P) = 1.4 Hz), 129.3 (d, *J*(C,P) = 5.0 Hz), 129.1 (d, *J*(C,P) = 8.2 Hz), 127.6 (d, *J*(C,P) = 4.8 Hz), 127.2 (d, *J*(C,P) = 1.2 Hz), 126.1 (d, *J*(C,P) = 7.9 Hz), 125.9 (s), 109.0 (d, *J*(C,P) = 1.0 Hz), 71.30 (s), 62.4 (dd, ^{1}*J*(C,P) = 15.5 Hz, ^{2}*J*(C,P) = 7.1 Hz), 50.5 (d, *J*(C,P) = 137.1 Hz), 34.4 (s), 30.3 (s), 29.8 (s), 16.3 (dd, ^{1}*J*(C,P) = 12.6 Hz, ^{2}*J*(C,P) = 5.8 Hz); ^{31}P{^{1}H} NMR

(160 MHz, $CDCl_3$, 25 °C, TMS): δ = 26.4. HRMS (ESI) *m*/*z*: calcd. for $C_{27}H_{38}O_5P$ $[M-H]^-$: 473.2457, found: 473.2451.

*Diethyl (anthracen-9-yl(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)phosphonate (**3aa**)*. According to the general procedure, work-up and flash column chromatography (R_f = 0.5, hexane/EtOAc: 2:1) gave product **3aa** (89.4 mg, 0.17 mmol, 84%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.54-8.57 (m, 1H), 8.44-8.45 (m, 1H), 8.36-8.38 (m, 1H), 7.94-8.06 (m, 2H), 7.31-7.57 (m, 4H), 7.24-7.25 (m, 2H), 6.21 (d, *J* = 32.7 Hz, 1H), 5.06 (s, 1H), 4.09-4.26 (m, 2H), 3.45-3.55 (m, 1H), 2.94-3.03 (m, 1H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.26 (s, 18H), 0.52 (t, *J* = 7.0 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 152.2 (d, *J*(C,P) = 1.3 Hz), 135.4 (s), 131.8 (s), 131.7 (s), 131.4 (s), 131.3 (s), 131.1 (s), 129.6 (s), 129.1 (s), 129.0 (s), 128.3 (s), 128.1 (d, *J*(C,P) = 4.2 Hz), 127.7 (d, *J*(C,P) = 2.9 Hz), 126.5 (s), 125.6 (d, *J*(C,P) = 8.4 Hz), 125.1 (s), 124.6 (s), 123.7 (s), 62.2 (dd, ^1J(C,P) = 113.8 Hz, ^2J(C,P) = 7.0 Hz), 44.2 (d, *J*(C,P) = 138.7 Hz), 34.4 (s), 30.2 (s), 16.2 (dd, ^1J(C,P) = 82.2 Hz, ^2J(C,P) = 6.0 Hz); ^{31}P{^{1}H} NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 26.9. HRMS (ESI) *m*/*z*: calcd. for $C_{33}H_{42}O_4P$ $[M+H]^+$: 533.2821, found: 533.2815.

*Diethyl ((4-hydroxy-3,5-dimethylphenyl)(phenyl)methyl)phosphonate (**3ab**)*. According to the general procedure, work-up and flash column chromatography (R_f = 0.5, Hexane/EtOAc: 5:1) gave product **3ab** (65.4 mg, 0.19 mmol, 94%) as a colorless oil.[14] ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.48-7.50 (m, 2H), 7.18-7.29 (m, 3H), 7.07-7.08 (m, 2H), 5.96 (s, 1H), 4.29 (d, *J* = 25.3 Hz, 1H), 3.77-4.03 (m, 4H), 2.16 (s, 6H), 1.12 (dt, *J* = 10.2, 7.1 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 152.0 (d, *J*(C,P) = 2.2 Hz), 137.3 (d, *J*(C,P) = 4.8 Hz), 129.4 (d, *J*(C,P) = 2.0 Hz), 129.3 (d, *J*(C,P) = 1.9 Hz), 128.5 (d, *J*(C,P) = 1.0 Hz), 127.5 (d, *J*(C,P) = 5.4 Hz), 126.9 (d, *J*(C,P) = 2.0 Hz), 123.9 (d, *J*(C,P) = 1.2 Hz), 62.7 (dd, ^1J(C,P) = 7.1 Hz, ^2J(C,P) = 2.7 Hz), 50.4 (d, *J*(C,P) = 137.7 Hz), 16.3 (d, *J*(C,P) = 8.9 Hz), 16.2 (s); ^{31}P{^{1}H} NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 25.7.

*Diethyl ((4-hydroxy-3,5-diisopropylphenyl)(phenyl)methyl)phosphonate (**3ac**)*. According to the general procedure, work-up and flash column chromatography (R_f = 0.4, Hexane/EtOAc: 5:1) gave product **3ac** (74.3 mg, 0.18 mmol, 92%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.51-7.53 (m, 2H), 7.25-7.30 (m, 2H), 7.18-7.22 (m, 3H), 5.59 (s, 1H), 4.35 (d, *J* = 25.4 Hz, 1H), 3.73-4.00 (m, 4H), 3.14-3.24 (m, 2H), 1.22 (d, J = 6.9 Hz, 12H), 1.05-1.12 (m, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 149.5 (s), 137.4 (d, J(C,P) = 4.9 Hz), 134.2 (s), 129.4 (d, J(C,P) = 7.8 Hz), 128.4 (d, J(C,P) = 1.3 Hz), 128.0 (d, J(C,P) = 5.2 Hz), 126.9 (d, J(C,P) = 2.2 Hz), 124.7 (d, J(C,P) = 8.2 Hz), 62.6 (dd, ^1J(C,P) = 33.4 Hz, ^2J(C,P) = 7.0 Hz), 51.1 (d, J(C,P) = 137.0 Hz), 27.1 (s), 22.8 (s), 16.2 (dd, ^1J(C,P) = 5.8 Hz, ^2J(C,P) = 3.1 Hz); $^{31}P\{^1H\}$ NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 25.8. HRMS (ESI) *m/z*: calcd. for $C_{23}H_{34}O_4P$ $[M+H]^+$: 405.2195, found: 405.2192.

*Diethyl ((2'-hydroxy-[1,1':3',1''-terphenyl]-5'-yl)(phenyl)methyl)phosphonate (**3ad**)*. According to the general procedure, work-up and flash column chromatography (R_f = 0.4, Hexane/EtOAc: 2:1) gave product **3ad** (81.2 mg, 0.17 mmol, 86%) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.53-7.56 (m, 6H), 7.44-7.48 (m, 6H), 7.32-7.39 (m, 4H), 7.22-7.25 (m, 1H), 5.41 (s, 1H), 4.43 (d, J = 25.2 Hz, 1H), 3.79-4.13 (m, 4H), 1.15 (dt, J = 20.3, 7.1 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 148.5 (s), 137.4 (s), 137.0 (d, J(C,P) = 4.9 Hz), 130.9 (d, J(C,P) = 8.1 Hz), 129.5 (s), 129.4 (s), 129.0 (d, J(C,P) = 5.4 Hz), 128.9 (s), 128.8 (d, J(C,P) = 1.2 Hz), 128.7 (d, J(C,P) = 1.1 Hz), 127.7 (s), 127.2 (d, J(C,P) = 2.0 Hz), 62.7 (dd, ^1J(C,P) = 7.1 Hz, ^2J(C,P) = 4.8 Hz), 50.6 (d, J(C,P) = 137.8 Hz), 16.3 (dd, ^1J(C,P) = 7.8, ^2J(C,P) = 5.8 Hz); $^{31}P\{^1H\}$ NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 25.2. HRMS (ESI) *m/z*: calcd. for $C_{29}H_{30}O_4P$ $[M+H]^+$: 473.1882, found: 473.1878.

*Diethyl ((4-hydroxyphenyl)diphenylmethyl)phosphonate (**3ae**)*. According to the general procedure, work-up and flash column chromatography (R_f = 0.5, Hexane/EtOAc: 2:1) gave product **3ae** (60.2 mg, 0.15 mmol, 76%) as a white solid.[17c] ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.81 (s, 1H), 7.22-7.31 (m, 10H), 7.05-7.08 (m, 2H), 6.60-6.63 (m, 2H), 3.97-4.07 (m, 2H), 3.77-3.87 (m, 2H), 1.11 (t, J = 7.1 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 155.7 (s), 141.6 (s), 141.5 (s), 131.8 (s), 131.7 (s), 131.6 (s), 131.5 (s), 130.7 (s), 130.6 (s), 127.8 (s), 126.9 (s), 115.3 (s), 63.6 (d, J(C,P) = 8.4 Hz), 62.3 (d, J(C,P) = 136.3 Hz), 16.2 (d, J(C,P) = 5.7 Hz); $^{31}P\{^1H\}$ NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 26.5.

*Dimethyl ((3,5-di-tert-butyl-4-hydroxyphenyl)(phenyl)methyl)phosphonate (**4a**)*. According to the general procedure, work-up and flash column chromatography (R_f = 0.5, Hexane/EtOAc: 5:1) gave product **4a** (74.2 mg, 0.18 mmol, 92%) as a colorless oil.[15b] ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ

= 7.52-7.54 (m, 2H), 7.30-7.34 (m, 4H), 7.22-7.26 (m, 1H), 5.15 (s, 1H), 4.36 (d, *J* = 25.3 Hz, 1H), 3.53 (dd, *J* = 10.6, 3.7 Hz, 6H), 1.41 (s, 18H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 153.0 (d, *J*(C,P) = 2.5 Hz), 137.1 (d, *J*(C,P) = 4.9 Hz), 135.9 (d, *J*(C,P) = 1.4 Hz), 129.4 (d, *J*(C,P) = 8.0 Hz), 128.6 (d, *J*(C,P) = 1.3 Hz), 127.1 (d, *J*(C,P) = 2.2 Hz), 126.7 (d, *J*(C,P) = 5.5 Hz), 126.1 (d, *J*(C,P) = 8.0 Hz), 53.3 (dd, ^1J(C,P) = 20.9 Hz, ^2J(C,P) = 7.1 Hz), 50.6 (d, *J*(C,P) = 136.8 Hz), 34.4 (s), 30.3 (s); $^{31}P\{^1H\}$ NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 28.2.

*Dipropyl ((3,5-di-tert-butyl-4-hydroxyphenyl)(phenyl)methyl)phosphonate (**4b**).* According to the general procedure, work-up and flash column chromatography (R_f = 0.4, Hexane/EtOAc: 5:1) gave product **4b** (85.6 mg, 0.19 mmol, 93%) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.53-7.55 (m, 2H), 7.20-7.33 (m, 5H), 5.13 (s, 1H), 4.35 (d, *J* = 25.4 Hz, 1H), 3.65-3.87 (m, 4H), 1.41-1.51 (m, 4H), 1.41 (s, 18H), 0.75 (dt, *J* = 9.4, 7.4 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 152.9 (d, *J*(C,P) = 2.5 Hz), 137.4 (d, *J*(C,P) = 4.9 Hz), 135.8 (d, *J*(C,P) = 1.5 Hz), 129.4 (d, *J*(C,P) = 7.9 Hz), 128.5 (d, *J*(C,P) = 1.2 Hz), 127.1 (d, *J*(C,P) = 5.5 Hz), 126.9 (d, *J*(C,P) = 2.2 Hz), 126.2 (d, *J*(C,P) = 7.9 Hz), 68.0 (dd, ^1J(C,P) = 23.6 Hz, ^2J(C,P) = 7.3 Hz), 51.1 (d, *J*(C,P) = 136.9 Hz), 34.4 (s), 30.3 (s), 23.8 (t, *J*(C,P) = 5.9 Hz), 9.9 (d, *J*(C,P) = 2.6 Hz); $^{31}P\{^1H\}$ NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 25.8. HRMS (ESI) *m/z*: calcd. for $C_{27}H_{42}O_4P$ $[M+H]^+$: 461.2821, found: 461.2815.

*Diisopropyl ((3,5-di-tert-butyl-4-hydroxyphenyl)(phenyl)methyl)phosphonate (**4c**).* According to the general procedure, work-up and flash column chromatography (R_f = 0.4, Hexane/EtOAc: 2:1) gave product **4c** (81.9 mg, 0.18 mmol, 89%) as a colorless oil.[15b] ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.55-7.57 (m, 2H), 7.34-7.35 (m, 2H), 7.28-7.32 (m, 2H), 7.19-7.23 (m, 1H), 5.13 (s, 1H), 4.40-4.53 (m, 2H), 4.26 (d, *J* = 25.5 Hz, 1H), 1.41 (s, 18H), 1.22 (d, *J* = 5.9 Hz, 6H), 0.85 (dd, *J* = 32.6, 6.2 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 152.9 (d, *J*(C,P) = 2.4 Hz), 137.7 (d, *J*(C,P) = 4.7 Hz), 135.7 (d, *J*(C,P) = 1.5 Hz), 129.5 (d, *J*(C,P) = 8.0 Hz), 128.4 (d, *J*(C,P) = 1.3 Hz), 127.4 (d, *J*(C,P) = 5.3 Hz), 126.8 (d, *J*(C,P) = 2.2 Hz), 126.3 (d, *J*(C,P) = 8.0 Hz), 70.9 (dd, ^1J(C,P) = 26.2 Hz, ^2J(C,P) = 7.3 Hz), 51.7 (d, *J*(C,P) = 138.3 Hz), 34.4 (s), 30.3 (s), 24.3 (dd, ^1J(C,P) = 15.0 Hz, ^2J(C,P) = 3.1 Hz), 23.2 (dd, ^1J(C,P) = 20.7 Hz, ^2J(C,P) = 5.7 Hz); $^{31}P\{^1H\}$ NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 24.3.

*Dibutyl ((3,5-di-tert-butyl-4-hydroxyphenyl)(phenyl)methyl)phosphonate (**4d**).* According to the general procedure, work-up and flash column chromatography (R_f = 0.5, Hexane/EtOAc: 2:1) gave product **4d** (89.8 mg, 0.18 mmol, 92%) as a colorless oil.[15a] ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C, TMS): δ = 7.53-7.55 (m, 2H), 7.28-7.33 (m, 4H), 7.20-7.24 (m, 1H), 5.13 (s, 1H), 4.34 (d, *J* = 25.3 Hz, 1H), 3.69-3.91 (m, 4H), 1.37-1.45 (m, 22H), 1.12-1.24 (m, 4H), 0.77-0.81 (m, 6H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$, 25 °C, TMS): δ = 152.9 (d, *J*(C,P) = 2.4 Hz), 137.4 (d, *J*(C,P) = 4.9 Hz), 135.8 (d, *J*(C,P) = 1.2 Hz), 129.4 (d, *J*(C,P) = 7.9 Hz), 128.4 (d, *J*(C,P) = 1.3 Hz), 127.1 (d, *J*(C,P) = 5.5 Hz), 126.9 (d, *J*(C,P) = 2.2 Hz), 126.2 (d, *J*(C,P) = 7.9 Hz), 68.2 (dd, ^{1}*J*(C,P) = 21.4 Hz, ^{2}*J*(C,P) =7.3 Hz), 51.1 (d, *J*(C,P) = 136.8 Hz), 34.4 (s), 32.4 (t, *J*(C,P) = 5.1 Hz), 30.3 (s), 18.6 (d, *J*(C,P) = 1.3 Hz), 13.5 (s); ^{31}P{^{1}H} NMR (160 MHz, CDCl$_3$, 25 °C, TMS): δ = 25.8.

*Dibenzyl ((3,5-di-tert-butyl-4-hydroxyphenyl)(phenyl)methyl)phosphonate (**4e**).* According to the general procedure, work-up and flash column chromatography (R_f = 0.4, Hexane/EtOAc: 2:1) gave product **4e** (95.6 mg, 0.17 mmol, 86%) as a colorless oil.[15b] ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C, TMS): δ = 7.54-7.56 (m, 2H), 7.22-7.37 (m, 11H), 7.01-7.11 (m, 4H), 5.15 (s, 1H), 4.69-4.91 (m, 4H), 4.44 (d, *J* = 25.6 Hz, 1H), 1.38 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$, 25 °C, TMS): δ = 153.1 (d, *J*(C,P) = 2.5 Hz), 137.0 (d, *J*(C,P) = 4.9 Hz), 136.5 (dd, ^{1}*J*(C,P) = 6.0 Hz, ^{2}*J*(C,P) = 5.1 Hz), 136.0 (d, *J*(C,P) = 1.4 Hz), 129.5 (d, *J*(C,P) = 8.0 Hz), 128.6 (d, *J*(C,P) = 1.3 Hz), 128.4 (d, *J*(C,P) = 2.3 Hz), 128.1 (d, *J*(C,P) = 2.7 Hz), 127.7 (d, *J*(C,P) = 13.3 Hz), 127.1 (d, *J*(C,P) = 2.3 Hz), 126.9 (d, *J*(C,P) = 5.5 Hz), 126.2 (d, *J*(C,P) = 8.2 Hz), 67.9 (dd, ^{1}*J*(C,P) = 9.2 Hz, ^{2}*J*(C,P) = 7.0 Hz), 51.3 (d, *J*(C,P) = 136.4 Hz), 34.4 (s), 30.3 (s); ^{31}P{^{1}H} NMR (160 MHz, CDCl$_3$, 25 °C, TMS): δ = 26.7.

*Bis(2,2,2-trifluoroethyl) ((3,5-di-tert-butyl-4-hydroxyphenyl)(phenyl)methyl)phosphonate (**4f**).* According to the general procedure, work-up and flash column chromatography (R_f = 0.5, hexane/EtOAc: 2:1) gave product **4f** (94.1 mg, 0.17 mmol, 87%) as a colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C, TMS): δ = 7.52-7.54 (m, 2H), 7.34-7.38 (m, 2H), 7.27-7.31 (m, 3H), 5.23 (s, 1H), 4.53 (d, *J* = 26.6 Hz, 1H), 4.19-4.33 (m, 2H), 3.77-3.94 (m, 2H), 1.41 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$, 25 °C, TMS): δ = 153.5 (d, *J*(C,P) = 2.8 Hz), 136.4 (d, *J*(C,P) = 1.7 Hz), 135.2 (d, *J*(C,P) = 4.8 Hz), 129.3 (d, *J*(C,P) = 8.7 Hz), 128.9 (d, *J*(C,P) = 1.4 Hz), 127.7 (d, *J*(C,P) = 2.4 Hz), 126.1 (d, *J*(C,P)

= 8.4 Hz), 124.8 (d, *J*(C,P) = 5.9 Hz), 122.5 (dd, ^{1}*J*(C,F) = 276.0 Hz, ^{2}*J*(C,P) = 9.0 Hz), 61.9-63.1 (m), 50.8 (d, *J*(C,P) = 137.1 Hz), 34.4 (s), 30.2 (s); ^{31}P{^{1}H} NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 28.7 (s); ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$, 25 °C, TMS): δ = -75.5 (d, *J*(F,P) = 6.6 Hz). HRMS (ESI) *m*/*z*: calcd. for $C_{25}H_{30}F_6O_4P$ $[M-H]^-$: 539.1786, found: 539.1783.

*Bis(1,1,1,3,3,3-hexafluoropropan-2-yl) ((3,5-di-tert-butyl-4-hydroxyphenyl)(phenyl)methyl) phosphonate (**4g**).* According to the general procedure, work-up and flash column chromatography (R_f = 0.6, hexane/EtOAc: 10:1) gave product **4g** (109.5 mg, 0.16 mmol, 81%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.44-7.46 (m, 2H), 7.19-7.31 (m, 5H), 5.16 (s, 1H), 4.83-4.99 (m, 2H), 4.57 (d, *J* = 27.3 Hz, 1H), 1.33 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 153.8 (d, *J*(C,P) = 3.2 Hz), 136.5 (d, *J*(C,P) = 2.0 Hz), 133.9 (d, *J*(C,P) = 4.4 Hz), 133.7 (d, *J*(C,F) = 390.3 Hz), 129.2 (d, *J*(C,P) = 9.1 Hz), 129.0 (d, *J*(C,P) = 156.7 Hz), 128.9 (d, *J*(C,P) = 1.3 Hz), 128.2 (s), 128.1 (d, *J*(C,P) = 1.9 Hz), 126.0 (d, *J*(C,P) = 8.8 Hz), 123.6 (d, *J*(C,P) = 6.3 Hz), 51.4 (d, *J*(C,P) = 134.8 Hz), 34.4 (s), 30.0 (s); ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 30.7 (s); ^{31}P{^{1}H} NMR (376 MHz, $CDCl_3$, 25 °C, TMS): δ = (-74.2)-(-73.9) (m). HRMS (ESI) *m*/*z*: calcd. for $C_{27}H_{30}F_{12}O_4P$ $[M+H]^+$: 677.1690, found: 677.1682.

*((3,5-Di-tert-butyl-4-hydroxyphenyl)(phenyl)methyl)diphenylphosphine oxide (**4h**).* According to the general procedure, work-up and flash column chromatography (R_f = 0.5, hexane/EtOAc: 1:1) gave product **4h** (87.4 mg, 0.18 mmol, 88%) as a colorless oil.[15b] ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.68-7.73 (m, 2H), 7.57-7.59 (m, 2H), 7.45-7.50 (m, 2H), 7.31-7.41 (m, 4H), 7.19-7.29 (m, 4H), 7.05-7.15 (m, 3H), 5.05 (s, 1H), 4.65 (d, *J* = 9.7 Hz, 1H), 1.29 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 152.8 (d, *J*(C,P) = 2.4 Hz), 137.8 (d, *J*(C,P) = 4.0 Hz), 135.5 (d, *J*(C,P) = 1.6 Hz), 133.1 (d, *J*(C,P) = 98.1 Hz), 132.5 (d, *J*(C,P) = 95.0 Hz), 131.5 (s), 131.4 (d, *J*(C,P) = 1.9 Hz), 131.3 (d, *J*(C,P) = 2.4 Hz), 131.1 (d, *J*(C,P) = 2.8 Hz), 129.9 (d, *J*(C,P) = 7.2 Hz), 128.5 (s), 128. 3 (d, *J*(C,P) = 11.3 Hz), 127.93 (d, *J*(C,P) = 11.6 Hz), 126.8 (s), 126.7 (s), 126.7 (d, *J*(C,P) = 5.3 Hz), 53.6 (d, *J*(C,P) = 65.6 Hz), 34.3 (s), 30.2 (s); ^{31}P{^{1}H} NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 31.2.

*((3,5-Di-tert-butyl-4-hydroxyphenyl)(phenyl)methyl)di-p-tolylphosphine oxide (**4i**).* According to the general procedure, work-up and flash column chromatography (R_f = 0.5, hexane/EtOAc: 2:1) gave

product **4i** (87.1 mg, 0.17 mmol, 83%) as a colorless oil.[15b] ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C, TMS): δ = 7.56-7.61 (m, 4H), 7.29-7.34 (m, 2H), 7.19-7.25 (m, 2H), 7.11-7.14 (m, 3H), 7.04-7.07 (m, 4H), 5.06 (s, 1H), 4.60 (d, *J* = 9.8 Hz, 1H), 2.29 (s, 6H), 1.29 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$, 25 °C, TMS): δ = 152.7 (d, *J*(C,P) = 2.5 Hz), 141.6 (d, *J*(C,P) = 2.8 Hz), 141.3 (d, *J*(C,P) = 2.8 Hz), 138.1 (d, *J*(C,P) = 3.8 Hz), 135.4 (d, *J*(C,P) = 1.7 Hz), 131.4 (d, *J*(C,P) = 19.1 Hz), 131.3 (d, *J*(C,P) = 1.2 Hz), 130.1 (d, *J*(C,P) = 100.8 Hz), 130.0 (d, *J*(C,P) = 7.2 Hz), 129.3 (d, *J*(C,P) = 97.3 Hz), 129.0 (d, *J*(C,P) = 11.6 Hz), 128.6 (d, *J*(C,P) = 11.8 Hz), 128.5 (s), 126.9 (s), 126.8 (d, *J*(C,P) = 5.8 Hz), 126.7 (d, *J*(C,P) = 0.9 Hz), 53.7 (d, *J*(C,P) = 65.7 Hz), 34.2 (s), 30.2 (s), 21.5 (d, *J*(C,P) = 8.4 Hz); ^{31}P{^{1}H} NMR (160 MHz, CDCl$_3$, 25 °C, TMS): δ = 31.7.

*((3,5-Di-tert-butyl-4-hydroxyphenyl)(phenyl)methyl)bis(4-methoxyphenyl)phosphine oxide (**4j**).* According to the general procedure, work-up and flash column chromatography (R$_f$ = 0.3, hexane/EtOAc: 2:1) gave product **4j** (94.5 mg, 0.17 mmol, 85%) as a colorless oil.[15b] ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C, TMS): δ = 7.57-7.62 (m, 4H), 7.30-7.36 (m, 2H), 7.11-7.23 (m, 3H), 7.06-7.07 (m, 2H), 6.76-6.85 (m, 4H), 5.08 (s, 1H), 4.57 (d, *J* = 10.2 Hz, 1H), 3.74 (s, 6H), 1.31 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$, 25 °C, TMS): δ = 161.9 (d, *J*(C,P) = 2.8 Hz), 161.8 (d, *J*(C,P) = 2.8 Hz), 152.7 (d, *J*(C,P) = 2.4 Hz), 138.1 (d, *J*(C,P) = 3.9 Hz), 135.5 (d, *J*(C,P) = 1.7 Hz), 133.2 (d, *J*(C,P) = 18.2 Hz), 133.1 (d, *J*(C,P) = 1.0 Hz), 129.9 (d, *J*(C,P) = 7.2 Hz), 128.4(s), 127.0 (d, *J*(C,P) = 5.3 Hz), 126.8 (d, *J*(C,P) = 5.8 Hz), 126.7 (d, *J*(C,P) = 0.9 Hz), 124.7 (d, *J*(C,P) = 104.7 Hz), 123.9 (d, *J*(C,P) = 101.4 Hz), 113.8 (d, *J*(C,P) = 12.3 Hz), 113.4 (d, *J*(C,P) = 12.5 Hz), 55.2 (d, *J*(C,P) = 1.5 Hz), 54.1 (d, *J*(C,P) = 66.4 Hz), 34.3 (s), 30.2 (s); ^{31}P{^{1}H} NMR (160 MHz, CDCl$_3$, 25 °C, TMS): δ = 31.4.

*((3,5-Di-tert-butyl-4-hydroxyphenyl)(phenyl)methyl)bis(3-fluorophenyl)phosphine oxide (**4k**).* According to the general procedure, work-up and flash column chromatography (R$_f$ = 0.4, hexane/EtOAc: 2:1) gave product **4k** (92.5 mg, 0.17 mmol, 87%) as a colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C, TMS): δ = 7.57-7.59 (m, 2H), 7.06-7.50 (m, 13H), 5.11 (s, 1H), 4.61 (d, *J* = 9.5 Hz, 1H), 1.31 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$, 25 °C, TMS): δ =162.5 (dd, ^{1}*J*(C,F) = 248.6 Hz, ^{2}*J*(C,P) = 32.6Hz), 162.4 (d, *J*(C,F) = 248.0 Hz), 153.0 (d, *J*(C,P) = 2.1 Hz), 137.0 (d, *J*(C,P) = 3.9 Hz), 135.9 (s), 134.9 (d, *J*(C,P) = 5.8 Hz), 134.7 (d, ^{1}*J*(C,P) = 93.4 Hz, ^{2}*J*(C,F) = 5.0 Hz), 134.2 (d, *J*(C,P) =

93.9 Hz), 130.2 (dd, ^1J(C,F) = 40.9 Hz, ^2J(C,P) = 7.3 Hz), 130.1 (dd, ^1J(C,F) = 41.4 Hz, ^2J(C,P) = 7.2 Hz), 129.8 (d, J(C,P) = 7.3 Hz), 128.7 (s), 127.1 (d, J(C,P) = 7.3 Hz), 126.9 (dd, ^1J(C,F) = 7.8 Hz, ^2J(C,P) = 2.6 Hz), 126.6 (d, J(C,P) = 6.1 Hz), 119.0 (d, J(C,P) = 2.2 Hz), 118.7 (d, J(C,P) = 2.0 Hz), 118.6 (s), 118.3 (d, J(C,P) = 1.6 Hz), 118.2 (s), 53.5 (d, J(C,P) = 66.7 Hz), 34.3 (s), 30.2 (s); ^{31}P{^{1}H} NMR (160 MHz, CDCl$_3$, 25 °C, TMS): δ = 29.4; ^{19}F{^{1}H} NMR (376 MHz, CDCl$_3$, 25 °C, TMS): δ = -111.4 (d, J(F,P) = 279.7 Hz). HRMS (ESI) *m*/*z*: calcd. for $C_{33}H_{36}F_2O_2P$ [M+H]$^+$: 533.2421, found: 533.2413.

((3,5-Di-tert-butyl-4-hydroxyphenyl)(phenyl)methyl)di(naphthalen-1-yl)phosphine oxide ***(4l)***. According to the general procedure, work-up and flash column chromatography (R$_f$ = 0.5, hexane/EtOAc: 2:1) gave product **4l** (96.5 mg, 0.16 mmol, 81%) as a colorless oil.[15b] ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C, TMS): δ = 8.59-8.61 (m, 2H), 7.88-7.95 (m, 4H), 7.67-7.79 (m, 3H), 7.49-7.54 (m, 1H), 7.17-7.36 (m, 9H), 6.81-6.82 (m, 2H), 4.93 (d, J = 8.8 Hz, 1H), 4.84 (s, 1H), 1.11 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$, 25 °C, TMS): δ = 152.7 (d, J(C,P) = 3.0 Hz), 139.6 (d, J(C,P) = 3.3 Hz), 135.2 (d, J(C,P) = 2.3 Hz), 134.8 (d, J(C,P) = 7.4 Hz), 134.0 (d, J(C,P) = 1.0 Hz), 133.9 (s), 133.2 (d, J(C,P) = 9.2 Hz), 132.7 (d, J(C,P) = 2.6 Hz), 132.3 (d, J(C,P) = 2.9 Hz), 131.7 (d, J(C,P) = 11.4 Hz), 131.5 (d, J(C,P) = 9.5 Hz), 130.5 (d, J(C,P) = 94.2 Hz), 130.2 (d, J(C,P) = 90.9 Hz), 130.0 (d, J(C,P) = 8.0 Hz), 128.9 (s), 128.6 (s), 128.2 (s), 127.5 (d, J(C,P) = 5.4 Hz), 127.1 (s), 127.0 (d, J(C,P) = 5.2 Hz), 126.8 (s), 126.7 (s), 126.6 (s), 126.3 (s), 126.2 (s), 125.9 (s), 124.2 (s), 124.0 (d, J(C,P) = 4.1 Hz), 123.9 (s), 54.1 (d, J(C,P) = 66.8 Hz), 34.0 (s), 30.0 (s); ^{31}P{^{1}H} NMR (160 MHz, CDCl$_3$, 25 °C, TMS): δ = 37.9.

((3,5-Di-tert-butyl-4-hydroxyphenyl)(o-tolyl)methyl)diphenylphosphine oxide ***(4m)***. According to the general procedure, work-up and flash column chromatography (R$_f$ = 0.5, hexane/EtOAc: 2:1) gave product **4m** (84.7 mg, 0.17 mmol, 83%) as a colorless oil.[15a] ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C, TMS): δ = 8.29-8.31 (m, 1H), 7.63-7.68 (m, 2H), 7.24-7.44 (m, 8H), 7.10-7.14 (m, 1H), 6.97-7.05 (m, 4H), 5.11 (s, 1H), 4.78 (d, J = 10.0 Hz, 1H), 2.26 (s, 3H), 1.27 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$, 25 °C, TMS): δ = 152.7 (d, J(C,P) = 2.7 Hz), 136.8 (d, J(C,P) = 2.8 Hz), 135.7 (d, J(C,P) = 9.7 Hz), 135.4 (d, J(C,P) = 1.8 Hz), 133.3 (d, J(C,P) = 99.1 Hz), 132.2 (d, J(C,P) = 94.4 Hz), 131.4 (d, J(C,P) = 12.7

Hz), 131.3 (d, *J*(C,P) = 5.8 Hz), 131.2 (d, *J*(C,P) = 8.5 Hz), 131.1 (d, *J*(C,P) = 2.6 Hz), 130.4 (s), 129.9 (d, *J*(C,P) = 6.0 Hz), 128.4 (d, *J*(C,P) = 11.3 Hz), 127.9 (d, *J*(C,P) = 11.5 Hz), 127.2 (d, *J*(C,P) = 5.6 Hz), 126.8 (s), 126.4 (s), 125.3 (d, *J*(C,P) = 5.8 Hz), 48.9 (d, *J*(C,P) = 67.1 Hz), 34.2 (s), 30.2 (s), 20.2 (s); ^{31}P{^{1}H} NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 32.4.

*((3,5-Di-tert-butyl-4-hydroxyphenyl)(3-methoxyphenyl)methyl)diphenylphosphine oxide (**4n**).* According to the general procedure, work-up and flash column chromatography (R_f = 0.5, hexane/EtOAc: 2:1) gave product **4n** (90.5 mg, 0.17 mmol, 86%) as a colorless oil.[15b] ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.70-7.75 (m, 2H), 7.45-7.50 (m, 2H), 7.32-7.39 (m, 4H), 7.24-7.28 (m, 2H), 7.18-7.19 (m, 2H), 7.09-7.13 (m, 3H), 6.67-6.70 (m, 1H), 5.08 (s, 1H), 4.63 (d, *J* = 9.7 Hz, 1H), 3.70 (s, 3H), 1.29 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 159.5 (s), 152.8 (d, *J*(C,P) = 2.4 Hz), 139.2 (d, *J*(C,P) = 3.9 Hz), 135.5 (d, *J*(C,P) = 1.7 Hz), 133.1 (d, *J*(C,P) = 98.1 Hz), 132.6 (d, *J*(C,P) = 95.0 Hz), 131.4 (d, *J*(C,P) = 19.6 Hz), 131.3 (d, *J*(C,P) = 2.6 Hz), 131.2 (d, *J*(C,P) = 2.7 Hz), 131.1 (d, *J*(C,P) = 2.7 Hz), 129.4 (s), 128.3 (d, *J*(C,P) = 11.4 Hz), 127.9 (d, *J*(C,P) = 11.6 Hz), 126.7 (d, *J*(C,P) = 6.0 Hz), 126.5 (d, *J*(C,P) = 5.4 Hz), 122.3 (d, *J*(C,P) = 7.2 Hz), 115.1 (d, *J*(C,P) = 7.3 Hz), 112.9 (d, *J*(C,P) = 1.1 Hz), 55.1 (s), 53.6 (d, *J*(C,P) = 65.5 Hz), 34.3 (s), 30.2 (s); ^{31}P{^{1}H} NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 31.1.

*((3,5-Di-tert-butyl-4-hydroxyphenyl)(3-fluorophenyl)methyl)diphenylphosphine oxide (**4o**).* According to the general procedure, work-up and flash column chromatography (R_f = 0.4, hexane/EtOAc: 2:1) gave product **4o** (87.4 mg, 0.17 mmol, 85%) as a colorless oil.[15b] ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.70-7.75 (m, 2H), 7.45-7.49 (m, 2H), 7.31-7.42 (m, 6H), 7.24-7.28 (m, 2H), 7.13-7.18 (m, 1H), 7.07-7.08 (m, 2H), 6.80-6.85 (m, 1H), 5.13 (s, 1H), 4.64 (d, *J* = 9.5 Hz, 1H), 1.30 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 162.6 (d, *J*(C,F) = 244.2 Hz), 152.9 (d, *J*(C,P) = 2.3 Hz), 140.2 (dd, ^{1}*J*(C,F) = 7.4 Hz, ^{2}*J*(C,P) = 3.8 Hz), 135.7 (d, *J*(C,P) = 1.5 Hz), 132.8 (d, *J*(C,P) = 98.8 Hz), 132.2 (d, *J*(C,P) = 95.2 Hz), 131.5 (d, *J*(C,P) = 2.6 Hz), 131.4 (d, *J*(C,P) = 16.6 Hz), 131.4 (s), 131.2 (d, *J*(C,P) = 2.7 Hz), 129.8 (d, *J*(C,P) = 8.3 Hz), 128.4 (d, *J*(C,P) = 11.4 Hz), 128.0 (d, *J*(C,P) = 11.6 Hz), 126.7 (d, *J*(C,P) = 5.9 Hz), 126.2 (d, *J*(C,P) = 5.4 Hz), 125.6 (dd, ^{1}*J*(C,F) = 7.1 Hz, ^{2}*J*(C,P) = 2.7 Hz), 116.9 (dd, ^{1}*J*(C,F) = 22.2 Hz, ^{2}*J*(C,P) = 7.3 Hz), 113.8 (d, *J*(C,F) = 20.9 Hz), 53.2

(d, *J*(C,P) = 67.0 Hz), 34.3 (s), 30.2 (s); $^{31}P\{^{1}H\}$ NMR (160 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 31.0; $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = -112.7 (s).

*((4-Bromophenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)diphenylphosphine oxide **(4p)**.* According to the general procedure, work-up and flash column chromatography (R_f = 0.4, hexane/EtOAc: 2:1) gave product **4p** (93.1 mg, 0.16 mmol, 81%) as a colorless oil.[15b] ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 7.69-7.73 (m, 2H), 7.40-7.49 (m, 5H), 7.32-7.38 (m, 5H), 7.26-7.29 (m, 2H), 7.03-7.04 (m, 2H), 5.09 (s, 1H), 4.61 (d, *J* = 9.5 Hz, 1H), 1.29 (s, 18H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 152.9 (d, *J*(C,P) = 2.3 Hz), 137.0 (d, *J*(C,P) = 3.9 Hz), 135.7 (d, *J*(C,P) = 1.5 Hz), 132.7 (d, *J*(C,P) = 98.8 Hz), 132.1 (d, *J*(C,P) = 95.2 Hz), 131.6 (s), 131.5 (d, *J*(C,P) = 6.0 Hz), 131.4 (s), 131.3 (s), 131.3 (s), 128.4 (d, *J*(C,P) = 11.4 Hz), 128.0 (s), 128.3 (d, *J*(C,P) = 11.6 Hz), 126.1 (d, *J*(C,P) = 5.9 Hz), 126.2 (d, *J*(C,P) = 5.4 Hz), 120.9 (d, *J*(C,P) = 1.7 Hz), 52.9 (d, *J*(C,P) = 65.6 Hz), 34.3 (s), 30.2 (s); $^{31}P\{^{1}H\}$ NMR (160 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 31.0.

*((3,5-Di-tert-butyl-4-hydroxyphenyl)(3-nitrophenyl)methyl)diphenylphosphine oxide **(4q)**.* According to the general procedure, work-up and flash column chromatography (R_f = 0.4, hexane/EtOAc: 2:1) gave product **4q** (95.2 mg, 0.18 mmol, 88%) as a colorless oil.[15b] ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 8.08-8.13 (m, 2H), 7.91-7.94 (m, 1H), 7.61-7.67 (m, 2H), 7.41-7.46 (m, 2H), 7.27-7.37 (m, 5H), 7.18-7.24 (m, 2H), 7.03-7.04 (m, 2H), 5.07 (s, 1H), 4.70 (d, *J* = 9.5 Hz, 1H), 1.23 (s, 18H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 153.2 (d, *J*(C,P) = 2.2 Hz), 148.0 (s), 139.9 (d, *J*(C,P) = 3.9 Hz), 136.0 (d, *J*(C,P) = 1.3 Hz), 135.9 (d, *J*(C,P) =5.6 Hz), 132.0 (d, *J*(C,P) = 97.7 Hz), 131.9 (d, *J*(C,P) = 2.7 Hz), 131.6 (d, *J*(C,P) = 95.6 Hz), 131.5 (d, *J*(C,P) = 2.5 Hz), 131.4 (s), 131.3 (s), 129.41 (s), 128.6 (d, *J*(C,P) = 11.5 Hz), 128.1 (d, *J*(C,P) = 11.7 Hz), 126.6 (d, *J*(C,P) = 6.0 Hz), 125.5 (d, *J*(C,P) = 5.2 Hz), 124.9 (d, *J*(C,P) = 8.1 Hz), 121.9 (d, *J*(C,P) = 1.0 Hz), 53.2 (d, *J*(C,P) = 64.6 Hz), 34.3 (s), 30.1 (s); $^{31}P\{^{1}H\}$ NMR (160 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 30.8.

*4-((3,5-Di-tert-butyl-4-hydroxyphenyl)(diphenylphosphoryl)methyl)benzaldehyde **(4r)**.* According to the general procedure, work-up and flash column chromatography (R_f = 0.5, hexane/EtOAc: 1:1) gave product **4r** (74.4 mg, 0.14 mmol, 71%) as a colorless oil.[15a] ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 9.91 (s, 1H), 7.69-7.78 (m, 6H), 7.47-7.51 (m, 2H), 7.27-7.43 (m, 6H), 7.08-7.09 (m, 2H), 5.13 (s, 1H), 4.74 (d, J = 9.2 Hz, 1H), 1.30 (s, 18H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 192.0 (s), 153.0 (d, J(C,P) = 2.3 Hz), 145.0 (d, J(C,P) = 3.8 Hz), 135.9 (d, J(C,P) = 1.5 Hz), 134.9 (d, J(C,P) = 1.1 Hz), 132.5 (d, J(C,P) =99.4 Hz), 132.0 (d, J(C,P) = 95.5 Hz), 131.7 (d, J(C,P) = 2.6 Hz), 131.4 (s), 131.3 (s), 130.5 (d, J(C,P) = 7.0 Hz), 129.9 (s), 128.5 (d, J(C,P) = 11.5 Hz), 128.1 (d, J(C,P) = 11.7 Hz), 126.7 (d, J(C,P) = 6.0 Hz), 125.7 (d, J(C,P) = 5.5 Hz), 53.8 (d, J(C,P) = 64.8 Hz), 34.3 (s), 30.2 (s); $^{31}P\{^1H\}$ NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 30.8.

*((3,5-Di-tert-butyl-4-hydroxyphenyl)(5-methylfuran-2-yl)methyl)diphenylphosphine oxide (**4s**).* According to the general procedure, work-up and flash column chromatography (R_f = 0.4, hexane/EtOAc: 2:1) gave product **4s** (79.1 mg, 0.16 mmol, 79%) as a colorless oil.[15b] ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.74-7.79 (m, 2H), 7.46-7.50 (m, 1H), 7.35-7.44 (m, 5H), 7.24-7.28 (m, 2H), 6.93-6.94 (m, 2H), 6.37-6.38 (m, 1H), 5.81-5.82 (m, 1H), 5.11 (s, 1H), 4.82 (d, J = 13.3 Hz, 1H), 2.14 (s, 3H), 1.29 (s, 18H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 153.0 (d, J(C,P) = 2.9 Hz), 151.0 (d, J(C,P) = 1.9 Hz), 148.0 (d, J(C,P) = 1.5 Hz), 135.4 (d, J(C,P) =2.2 Hz), 132.1 (d, J(C,P) = 116.7 Hz), 131.9 (d, J(C,P) = 96.1 Hz), 131.8 (s), 131.7 (s), 131.6 (d, J(C,P) = 16.1 Hz), 131.3 (d, J(C,P) = 2.7 Hz), 128.3 (d, J(C,P) = 11.4 Hz), 127.8 (d, J(C,P) = 11.6 Hz), 126.8 (d, J(C,P) = 4.9 Hz), 123.9 (d, J(C,P) = 5.2 Hz), 110.3 (d, J(C,P) = 4.3 Hz), 106.8 (d, J(C,P) = 1.4 Hz), 48.0 (d, J(C,P) = 65.8 Hz), 34.2 (s), 30.1 (s), 13.5 (s); $^{31}P\{^1H\}$ NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 29.7.

*(Rp+Rc/Sp+Sc)-6-((3,5-di-tert-butyl-4-hydroxyphenyl)(phenyl)methyl)-6H-dibenzo[c,e][1,2]oxaphosphinine 6-oxide (**5a**).* According to the general procedure, work-up and flash column chromatography (R_f = 0.4, hexane/EtOAc: 2:1) gave product **5a** (45.9 mg, 0.09 mmol, 44%) as a white solid. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.85-7.90 (m, 2H), 7.59-7.62 (m, 1H), 7.52-7.54 (m, 2H), 7.18-7.40 (m, 7H), 6.95-6.97 (m, 3H), 5.07 (s, 1H), 4.33 (d, J = 18.2 Hz, 1H), 1.28 (s, 18H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 153.1 (d, J(C,P) = 3.2 Hz), 150.0 (d, J(C,P) = 8.2 Hz), 136.0 (d, J(C,P) = 6.7 Hz), 135.7 (d, J(C,P) =2.0 Hz), 135.7 (s), 133.1 (d, J(C,P) = 2.1 Hz), 132.1 (d, J(C,P) = 8.5 Hz), 130.5 (s), 129.6 (d, J(C,P) = 7.1 Hz), 128.6 (s), 127.9 (d, J(C,P) = 12.4 Hz), 127.2 (d, J(C,P) = 2.0 Hz), 126.6 (d, J(C,P) = 6.7 Hz), 125.0 (s), 124.8 (d, J(C,P) = 4.2 Hz), 124.3 (s), 123.3 (d, J(C,P) = 10.0 Hz), 123.0 (d, J(C,P) = 108.7 Hz), 122.4 (s), 120.4 (d, J(C,P) = 6.4 Hz), 52.9 (d,

J(C,P) = 87.8 Hz), 34.2 (s), 30.1 (s); ^{31}P{^{1}H} NMR (160 MHz, CDCl$_3$, 25 ^{o}C, TMS): δ = 34.1. HRMS (ESI) *m*/*z*: calcd. for $C_{33}H_{36}O_3P$ [M+H]$^+$: 511.2402, found: 511.2398.

*(Sp+Rc/Rp+Sc)-6-((3,5-di-tert-butyl-4-hydroxyphenyl)(phenyl)methyl)-6H-dibenzo[c,e][1,2]oxaphosphinine 6-oxide (**5a'**).* According to the general procedure, work-up and flash column chromatography (R_f = 0.5, hexane/EtOAc: 2:1) gave product **5a'** (46.1 mg, 0.09 mmol, 45%) as a white solid. ^{1}H NMR (400 MHz, CDCl$_3$, 25 ^{o}C, TMS): δ = 7.80-7.85 (m, 2H), 7.51-7.53 (m, 2H), 7.52-7.54 (m, 2H), 7.17-7.36 (m, 6H), 7.00-7.04 (m, 3H), 5.06 (s, 1H), 4.34 (d, J = 15.5 Hz, 1H), 1.29 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$, 25 ^{o}C, TMS): δ = 153.0 (d, J(C,P) = 3.0 Hz), 150.2 (d, J(C,P) = 8.7 Hz), 136.1 (d, J(C,P) = 6.6 Hz), 135.6 (s), 135.5 (d, J(C,P) =2.4 Hz), 133.2 (d, J(C,P) = 2.2 Hz), 131.6 (d, J(C,P) = 8.9 Hz), 130.4 (s), 129.9 (d, J(C,P) = 7.9 Hz), 128.7 (s), 128.2 (d, J(C,P) = 12.6 Hz), 127.3 (d, J(C,P) = 1.8 Hz), 126.3 (d, J(C,P) = 6.1 Hz), 125.1 (s), 125.0 (d, J(C,P) = 3.8 Hz), 124.3 (s), 124.2 (d, J(C,P) = 153.3 Hz), 123.3 (d, J(C,P) = 9.8 Hz), 122.2 (d, J(C,P) = 9.9 Hz), 120.4 (d, J(C,P) = 6.5 Hz), 53.5 (d, J(C,P) = 88.4 Hz), 34.2 (s), 30.1 (s); ^{31}P{^{1}H} NMR (160 MHz, CDCl$_3$, 25 ^{o}C, TMS): δ = 33.8. HRMS (ESI) *m*/*z*: calcd. for $C_{33}H_{36}O_3P$ [M+H]$^+$: 511.2402, found: 511.2397.

*(Rp+Rc/Sp+Sc)-6-((3,5-di-tert-butyl-4-hydroxyphenyl)(4-ethylphenyl)methyl)-6H-dibenzo[c,e][1,2] oxaphosp hinine 6-oxide (**5b**).* According to the general procedure, work-up and flash column chromatography (R_f = 0.4, hexane/EtOAc: 2:1) gave product **5b** (48.7 mg, 0.09 mmol, 45%) as a colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$, 25 ^{o}C, TMS): δ = 7.83-7.88 (m, 2H), 7.58-7.62 (m, 1H), 7.24-7.43 (m, 5H), 7.13-7.21 (m, 3H), 6.96-7.00 (m, 3H), 5.05 (s, 1H), 4.30 (d, J = 18.4 Hz, 1H), 2.59-2.65 (m, 2H), 1.28 (s, 18H), 1.22 (t, J = 7.6 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$, 25 ^{o}C, TMS): δ = 153.0 (d, J(C,P) = 3.1 Hz), 150.1 (d, J(C,P) = 8.3 Hz), 143.1 (d, J(C,P) = 2.3 Hz), 136.1 (d, J(C,P) = 6.8 Hz), 135.7 (d, J(C,P) = 2.1 Hz), 133.0 (d, J(C,P) = 2.1 Hz), 132.8 (d, J(C,P) = 6.0 Hz), 132.1 (d, J(C,P) = 8.5 Hz), 130.5 (s), 129.5 (d, J(C,P) = 6.9 Hz), 128.2 (s), 128.1 (s), 127.9 (d, J(C,P) = 12.4 Hz), 126.6 (d, J(C,P) = 6.9 Hz), 125.0 (d, J(C,P) = 3.9Hz), 124.2 (d, J(C,P) = 116.7 Hz), 124.2 (s), 123.2 (d, J(C,P) = 9.9 Hz), 122.5 (d, J(C,P) = 10.0 Hz), 120.4 (d, J(C,P) = 6.3 Hz), 52.6 (d, J(C,P) = 87.6 Hz), 34.2 (s), 30.1 (s), 28.5 (s), 15.5 (s); ^{31}P{^{1}H} NMR (160 MHz, CDCl$_3$, 25 ^{o}C, TMS): δ = 34.3. HRMS (ESI) *m*/*z*: calcd. for $C_{35}H_{40}O_3P$ [M+H]$^+$: 539.2715, found: 539.2710.

*(Sp+Rc/Rp+Sc)-6-((3,5-di-tert-butyl-4-hydroxyphenyl)(4-ethylphenyl)methyl)-6H-dibenzo[c,e][1,2] oxaphosp hinine 6-oxide (**5b'**)*. According to the general procedure, work-up and flash column chromatography (R_f = 0.5, hexane/EtOAc: 2:1) gave product **5b'** (49.1 mg, 0.09 mmol, 45%) as a colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$, 25 ^{o}C, TMS): δ = 7.79-7.84 (m, 2H), 7.57-7.67 (m, 2H), 7.40-7.43 (m, 2H), 7.29-7.36 (m, 2H), 7.15-7.20 (m, 1H), 7.09-7.11 (m, 2H), 6.96-7.-02 (m, 3H), 5.05 (s, 1H), 4.32 (d, *J* = 15.8 Hz, 1H), 2.57-2.67 (m, 2H), 1.29 (s, 18H), 1.18 (t, *J* = 7.6 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$, 25 ^{o}C, TMS): δ = 153.0 (d, *J*(C,P) = 3.0 Hz), 150.2 (d, *J*(C,P) = 8.5 Hz), 143.3 (d, *J*(C,P) = 2.0 Hz), 136.1 (d, *J*(C,P) = 6.5 Hz), 135.5 (d, *J*(C,P) = 2.3 Hz), 133.1 (s), 132.6 (d, *J*(C,P) = 3.6 Hz), 131.7 (d, *J*(C,P) = 9.0 Hz), 130.4 (s), 129.8 (d, *J*(C,P) = 7.9 Hz), 128.1 (d, *J*(C,P) = 12.6 Hz), 126.3 (d, *J*(C,P) = 6.2 Hz), 125.3 (d, *J*(C,P) = 7.2 Hz), 124.9 (s), 124.3 (s), 123.2 (d, *J*(C,P) = 9.8 Hz), 123.1 (d, *J*(C,P) = 116.2 Hz), 122.3 (d, *J*(C,P) = 9.9 Hz), 122.3 (s), 120.4 (d, *J*(C,P) = 6.5 Hz), 53.2 (d, *J*(C,P) = 88.4 Hz), 34.2 (s), 30.1 (s), 28.5 (s), 15.6 (s); ^{31}P{^{1}H} NMR (160 MHz, CDCl$_3$, 25 ^{o}C, TMS): δ = 34.0. HRMS (ESI) *m/z*: calcd. for $C_{35}H_{40}O_3P$ [M+H]$^+$: 539.2715, found: 539.2708.

*(Rp+Rc/Sp+Sc)-6-((3,5-di-tert-butyl-4-hydroxyphenyl)(3-methoxyphenyl)methyl)-6H-dibenzo[c,e][1,2]oxaphosphinine 6-oxide (**5c**)*. According to the general procedure, work-up and flash column chromatography (R_f = 0.5, hexane/EtOAc: 2:1) gave product **5c** (42.1 mg, 0.08 mmol, 39%) as a colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$, 25 ^{o}C, TMS): δ = 7.84-7.89 (m, 2H), 7.59-7.63 (m, 1H), 7.37-7.42 (m, 1H), 7.28-7.32 (m, 2H), 7.18-7.23 (m, 2H), 7.08-7.11 (m, 2H), 6.97-7.00 (m, 3H), 6.79-6.81 (m, 1H), 5.08 (s, 1H), 4.31 (d, *J* = 18.3 Hz, 1H), 3.77 (s, 3H), 1.29 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$, 25 ^{o}C, TMS): δ = 159.6 (d, *J*(C,P) = 1.2 Hz), 153.1 (d, *J*(C,P) = 3.1 Hz), 150.1 (d, *J*(C,P) = 8.3 Hz), 136.1 (d, *J*(C,P) = 6.7 Hz), 135.7 (d, *J*(C,P) = 2.2 Hz), 133.1 (d, *J*(C,P) = 2.1 Hz), 132.1 (d, *J*(C,P) = 8.5 Hz), 130.5 (s), 129.5 (d, *J*(C,P) = 1.3 Hz), 127.9 (d, *J*(C,P) = 12.5 Hz), 126.6 (d, *J*(C,P) = 6.8 Hz), 125.0 (s), 125.0 (s), 124.6 (d, *J*(C,P) = 4.3 Hz), 124.3 (s), 124.1 (d, *J*(C,P) = 112.7 Hz), 123.2 (d, *J*(C,P) = 9.9 Hz), 122.4 (d, *J*(C,P) = 9.9 Hz), 122.1 (d, *J*(C,P) = 5.9Hz), 120.4 (d, *J*(C,P) = 6.4 Hz), 114.9 (d, *J*(C,P) = 7.0 Hz), 113.3 (d, *J*(C,P) = 2.1 Hz), 55.2 (s), 53.0 (d, *J*(C,P) = 87.6 Hz), 34.2 (s), 30.1 (s); ^{31}P{^{1}H} NMR (160 MHz, CDCl$_3$, 25 ^{o}C, TMS): δ = 34.0. HRMS (ESI) *m/z*: calcd. for $C_{34}H_{38}O_4P$ [M+H]$^+$: 541.2508, found: 541.2503.

*(Sp+Rc/Rp+Sc)-6-((3,5-di-tert-butyl-4-hydroxyphenyl)(3-methoxyphenyl)methyl)-6H-dibenzo[c,e][1,2]oxaphosphinine 6-oxide (**5c'**).* According to the general procedure, work-up and flash column chromatography ($R_f = 0.4$, hexane/EtOAc: 2:1) gave product ***5c'*** (49.8 mg, 0.09 mmol, 46%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.80-7.85 (m, 2H), 7.65-7.70 (m, 1H), 7.58-7.62 (m, 1H), 7.30-7.38 (m, 2H), 7.13-7.22 (m, 3H), 7.00-7.03 (m, 4H), 6.76-6.78 (m, 1H), 5.07 (s, 1H), 4.32 (d, J = 15.7 Hz, 1H), 3.75 (s, 3H), 1.30 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 159.6 (s), 153.0 (d, J(C,P) = 3.0 Hz), 150.1 (d, J(C,P) = 8.7 Hz), 136.9 (d, J(C,P) = 3.2 Hz), 136.1 (d, J(C,P) = 6.6 Hz), 135.6 (d, J(C,P) = 2.3 Hz), 133.2 (d, J(C,P) = 2.1 Hz), 131.7 (d, J(C,P) = 9.0 Hz), 130.4 (s), 129.6 (s), 128.2 (d, J(C,P) = 12.6 Hz), 126.3 (d, J(C,P) = 6.2 Hz), 124.9 (s), 124.8 (s), 124.3 (s), 124.2 (d, J(C,P) = 116.6 Hz), 123.3 (d, J(C,P) = 9.7 Hz), 122.3 (d, J(C,P) = 2.1 Hz), 122.2 (d, J(C,P) = 4.5Hz), 120.3 (d, J(C,P) = 6.5 Hz), 115.3 (d, J(C,P) = 8.2 Hz), 113.3 (d, J(C,P) = 1.8 Hz), 55.2 (s), 53.5 (d, J(C,P) = 88.4 Hz), 34.2 (s), 30.1 (s); ^{31}P{^{1}H} NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 33.6. HRMS (ESI) *m/z*: calcd. for $C_{34}H_{38}O_4P$ [M+H]$^+$: 541.2508, found: 541.2501.

*(Rp+Rc/Sp+Sc)-6-((3,5-di-tert-butyl-4-hydroxyphenyl)(3-nitrophenyl)methyl)-6H-dibenzo[c,e][1,2]oxaphosphinine 6-oxide (**5d**).* According to the general procedure, work-up and flash column chromatography ($R_f = 0.5$, hexane/EtOAc: 2:1) gave product **5d ;**(46.5 mg, 0.08 mmol, 42%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.86-7.91 (m, 2H), 7.59-7.64 (m, 2H), 7.53-7.54 (m, 1H), 7.19-7.40 (m, 6H), 7.00-7.02 (m, 1H), 6.93-6.94 (m, 2H), 5.12 (s, 1H), 4.26 (d, J = 17.8 Hz, 1H), 1.29 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 153.3 (d, J(C,P) = 3.1 Hz), 149.9 (d, J(C,P) = 8.4 Hz), 138.0 (d, J(C,P) = 5.9 Hz), 136.1 (d, J(C,P) = 6.8 Hz), 135.9 (d, J(C,P) = 2.1 Hz), 133.3 (d, J(C,P) = 2.2 Hz), 132.7 (d, J(C,P) = 7.6 Hz), 132.1 (d, J(C,P) = 8.4 Hz), 130.7 (s), 130.4 (d, J(C,P) = 1.9 Hz), 130.1 (d, J(C,P) = 1.5 Hz), 128.2 (d, J(C,P) = 6.3 Hz), 128.0 (d, J(C,P) = 11.6 Hz), 126.6 (d, J(C,P) = 6.7 Hz), 125.1 (s), 124.5 (s), 124.1 (d, J(C,P) = 3.9 Hz), 123.7 (d, J(C,P) = 118.6 Hz), 123.3 (d, J(C,P) = 9.9 Hz), 122.5 (d, J(C,P) = 1.1 Hz), 122.4 (d, J(C,P) = 10.1Hz), 120.4 (d, J(C,P) = 6.5 Hz), 52.3 (d, J(C,P) = 87.3 Hz), 34.2 (s), 30.0 (s); ^{31}P{^{1}H} NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 33.5. HRMS (ESI) *m/z*: calcd. for $C_{33}H_{35}NO_5P$ [M+H]$^+$: 556.2253, found: 556.2246.

*(Sp+Rc/Rp+Sc)-6-((3,5-di-tert-butyl-4-hydroxyphenyl)(3-nitrophenyl)methyl)-6H-dibenzo[c,e][1,2]oxaphosphinine 6-oxide (**5d'**).* According to the general procedure, work-up and flash column chromatography ($R_f = 0.4$, hexane/EtOAc: 2:1) gave product **5d'** (49.9 mg, 0.09 mmol, 46%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 7.80-7.87 (m, 2H), 7.62-7.73 (m, 3H), 7.50-7.52 (m, 1H), 7.31-7.41 (m, 3H), 7.18-7.22 (m, 2H), 7.00-7.03 (m, 1H), 6.93-6.94 (m, 2H), 5.09 (s, 1H), 4.31 (d, *J* = 15.6 Hz, 1H), 1.29 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 153.2 (d, *J*(C,P) = 3.0 Hz), 150.1 (d, *J*(C,P) = 8.6 Hz), 137.9 (d, *J*(C,P) = 3.0 Hz), 136.2 (d, *J*(C,P) = 6.5 Hz), 150.1 (d, *J*(C,P) = 8.6 Hz), 137.9 (d, *J*(C,P) = 3.0 Hz), 136.2 (d, *J*(C,P) = 6.5 Hz), 135.7 (d, *J*(C,P) = 2.3 Hz), 133.4 (d, *J*(C,P) = 2.2 Hz), 133.1 (d, *J*(C,P) = 9.0 Hz), 131.7 (d, *J*(C,P) = 3.0 Hz), 130.4 (d, *J*(C,P) = 1.8 Hz), 130.1 (d, *J*(C,P) = 1.0 Hz), 128.4 (d, *J*(C,P) = 3.9 Hz), 128.3 (d, *J*(C,P) = 1.5 Hz), 126.2 (d, *J*(C,P) = 6.0 Hz), 124.7 (d, *J*(C,P) = 55.9 Hz), 124.3 (d, *J*(C,P) = 7.4 Hz), 123.7 (d, *J*(C,P) = 109.8 Hz), 123.4 (d, *J*(C,P) = 9.8 Hz), 122.1 (d, *J*(C,P) = 9.8 Hz), 120.3 (d, *J*(C,P) = 6.6Hz), 53.1 (d, *J*(C,P) = 88.5 Hz), 34.2 (s), 30.1 (s); ^{31}P{^{1}H} NMR (160 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 33.1. HRMS (ESI) *m/z*: calcd. for $C_{33}H_{35}NO_5P$ $[M+H]^+$: 556.2253, found: 556.2249.

*(Rp+Rc/Sp+Sc)-6-((3,5-di-tert-butyl-4-hydroxyphenyl)(4-fluorophenyl)methyl)-6H-dibenzo[c,e][1,2]oxaphosphinine 6-oxide (**5e**).* According to the general procedure, work-up and flash column chromatography ($R_f = 0.4$, hexane/EtOAc: 2:1) gave product **5e** (48.5 mg, 0.09 mmol, 46%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 7.86-7.91 (m, 2H), 7.60-7.64 (m, 1H), 7.50-7.53 (m, 2H), 7.20-7.38 (m, 4H), 6.95-7.03 (m, 3H), 6.90-6.91 (m, 2H), 5.10 (s, 1H), 4.30 (d, *J* = 18.0 Hz, 1H), 1.28 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 153.2 (d, *J*(C,F) = 244.5 Hz, *J*(C,P) = 3.1 Hz), 150.1 (d, *J*(C,P) = 8.6 Hz), 153.2 (d, *J*(C,P) = 3.1 Hz), 149.9 (d, *J*(C,P) = 8.3 Hz), 136.0 (d, *J*(C,P) = 6.8 Hz), 135.8 (d, *J*(C,P) = 2.2 Hz), 133.2 (d, *J*(C,P) = 2.1 Hz), 132.1 (d, *J*(C,P) = 8.4 Hz), 131.5 (d, *J*(C,P) = 3.2 Hz), 131.4 (d, *J*(C,P) = 3.0 Hz), 127.9 (d, *J*(C,P) = 12.5 Hz), 126.5 (d, *J*(C,P) = 6.7 Hz), 125.1 (s), 124.5 (d, *J*(C,P) = 4.7 Hz), 123.9 (d, *J*(C,P) = 117.8 Hz), 123.3 (d, *J*(C,P) = 10.0 Hz), 122.4 (d, *J*(C,P) = 10.0 Hz), 122.4 (d, *J*(C,P) = 10.1 Hz), 120.3 (d, *J*(C,P) = 6.4 Hz), 115.5 (d, *J*(C,P) = 1.1 Hz), 51.8 (d, *J*(C,P) = 88.0 Hz), 34.2 (s), 30.1 (s); ^{31}P{^{1}H} NMR (160 MHz,

$CDCl_3$, 25 °C, TMS): δ = 34.01 (d, *J*(P,F) = 3.0 Hz). HRMS (ESI) *m*/*z*: calcd. for $C_{33}H_{35}FO_3P$ $[M+H]^+$: 529.2308, found: 529.2305.

*(Sp+Rc/Rp+Sc)-6-((3,5-di-tert-butyl-4-hydroxyphenyl)(4-fluorophenyl)methyl)-6H-dibenzo[c,e][1,2]oxaphosphinine 6-oxide (**5e'**).* According to the general procedure, work-up and flash column chromatography (R_f = 0.4, hexane/EtOAc: 2:1) gave product **5e'** (41.2 mg, 0.08 mmol, 39%) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.80-7.86 (m, 2H), 7.62-7.66 (m, 2H), 7.48-7.52 (m, 2H), 7.33-7.39 (m, 2H), 7.17-7.22 (m, 1H), 6.94-7.03 (m, 5H), , 5.08 (s, 1H), 4.34 (d, *J* = 15.7 Hz, 1H), 1.29 (s, 18H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 162.1 (dd, ^1J(C,F) = 244.8 Hz, ^2J(C,P) = 2.2 Hz), 153.1 (d, *J*(C,P) = 3.0 Hz), 150.1 (d, *J*(C,P) = 8.6 Hz), 136.1 (d, *J*(C,P) = 6.5 Hz), 135.7 (d, *J*(C,P) = 2.4 Hz), 133.3 (d, *J*(C,P) = 2.2 Hz), 131.6 (d, *J*(C,P) = 2.0 Hz), 131.5 (d, *J*(C,P) = 3.0 Hz), 131.4 (d, *J*(C,P) = 3.3 Hz), 130.5 (s), 128.3 (d, *J*(C,P) = 12.6 Hz), 126.2 (d, *J*(C,P) = 6.1 Hz), 125.0 (s), 124.9 (d, *J*(C,P) = 7.3 Hz), 124.4 (s), 124.0 (d, *J*(C,P) = 117.0 Hz), 123.3 (d, *J*(C,P) = 9.8 Hz), 122.2 (d, *J*(C,P) = 9.9 Hz), 120.4 (d, *J*(C,P) = 6.5 Hz), 115.7 (d, *J*(C,P) = 21.2 Hz), 52.6 (d, *J*(C,P) = 88.8 Hz), 34.2 (s), 30.1 (s); $^{31}P\{^1H\}$ NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 33.5 (d, *J*(P,F) = 3.0 Hz). HRMS (ESI) *m*/*z*: calcd. for $C_{33}H_{35}FO_3P$ $[M+H]^+$: 529.2308, found: 529.2301.

*(Rp+Rc/Sp+Sc)-6-((4-bromophenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)-6H-dibenzo[c,e][1,2]oxaphosphinine 6-oxide (**5f**).* According to the general procedure, work-up and flash column chromatography (R_f = 0.5, hexane/EtOAc: 2:1) gave product **5f** (42.3 mg, 0.07 mmol, 36%) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.79-7.83 (m, 2H), 7.53-7.57 (m, 1H), 7.37-7.39 (m, 4H), 7.13-7.30 (m, 4H), 6.89-6.91 (m, 1H), 6.82-6.83 (m, 2H), 5.03 (s, 1H), 4.19 (d, *J* = 17.9 Hz, 1H), 1.21 (s, 18H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 153.2 (d, *J*(C,P) = 3.0 Hz), 149.8 (d, *J*(C,P) = 8.3 Hz), 136.1 (d, *J*(C,P) = 6.8 Hz), 135.9 (d, *J*(C,P) = 2.2 Hz), 134.9 (d, *J*(C,P) = 5.8 Hz), 133.3 (s), 132.1 (d, *J*(C,P) = 8.4 Hz), 131.7 (s), 131.3 (d, *J*(C,P) = 7.0 Hz), 130.7 (s), 128.0 (d, *J*(C,P) = 12.4 Hz), 126.5 (d, *J*(C,P) = 6.6 Hz), 125.1 (s), 124.5 (s), 124.2 (d, *J*(C,P) = 4.0 Hz), 123.9 (d, *J*(C,P) = 118.2 Hz), 123.4 (d, *J*(C,P) = 10.0 Hz), 122.4 (d, *J*(C,P) = 10.1 Hz), 121.4 (d, *J*(C,P) = 2.5 Hz), 120.3 (d, *J*(C,P) = 6.5 Hz), 52.0 (d, *J*(C,P) = 87.7 Hz), 34.2 (s), 30.1 (s); $^{31}P\{^1H\}$ NMR (160 MHz,

$CDCl_3$, 25 °C, TMS): δ = 33.7. HRMS (ESI) *m/z*: calcd. for $C_{33}H_{35}BrO_3P$ $[M+H]^+$: 589.1507, found: 589.1500.

*(Sp+Rc/Rp+Sc)-6-((4-bromophenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)-6H-dibenzo[c,e][1,2]oxaphosphinine 6-oxide (**5f'**).* According to the general procedure, work-up and flash column chromatography ($R_f = 0.4$, hexane/EtOAc: 2:1) gave product **5f'** (56.4 mg, 0.10 mmol, 48%) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.72-7.79 (m, 2H), 7.53-7.63 (m, 2H), 7.24-7.34 (m, 6H), 7.11-7.15 (m, 1H), 6.92-6.94 (m, 1H), 6.85-6.86 (m, 2H), 5.01 (s, 1H), 4.24 (d, *J* = 15.5 Hz, 1H), 1.21 (s, 18H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 153.1 (d, *J*(C,P) = 3.1 Hz), 150.0 (d, *J*(C,P) = 8.6 Hz), 136.1 (d, *J*(C,P) = 6.6 Hz), 135.7 (d, *J*(C,P) = 2.3 Hz), 134.8 (d, *J*(C,P) = 3.3 Hz), 133.4 (d, *J*(C,P) = 2.2 Hz), 131.8 (s), 131.6 (s), 131.5 (s), 130.5 (s), 129.1 (s), 128.3 (d, *J*(C,P) = 12.6 Hz), 126.2 (d, *J*(C,P) = 6.1 Hz), 125.0 (s), 124.5 (d, *J*(C,P) = 4.6 Hz), 124.0 (d, *J*(C,P) = 115.6 Hz), 123.3 (d, *J*(C,P) = 2.0 Hz), 122.1 (d, *J*(C,P) = 9.8 Hz), 121.5 (d, *J*(C,P) = 2.3 Hz), 120.3 (d, *J*(C,P) = 6.6 Hz), 52.9 (d, *J*(C,P) = 88.7 Hz), 34.2 (s), 30.1 (s); $^{31}P\{^1H\}$ NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 33.2. HRMS (ESI) *m/z*: calcd. for $C_{33}H_{35}BrO_3P$ $[M+H]^+$: 589.1507, found: 589.1499.

*(Rp+Rc/Sp+Sc)-6-((2-bromophenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)-6H-dibenzo[c,e][1,2]oxaphosphinine 6-oxide (**5g**).* According to the general procedure, work-up and flash column chromatography ($R_f = 0.5$, hexane/EtOAc: 2:1) gave product **5g** (41.1 mg, 0.07 mmol, 35%) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.38-8.41 (m, 1H), 7.90-7.94 (m, 2H), 7.61-7.65 (m, 1H), 7.47-7.49 (m, 1H), 7.24-7.42 (m, 5H), 7.10-7.14 (m, 1H), 7.00-7.01 (m, 2H), 6.88-6.90 (m, 1H), 5.11 (s, 1H), 4.92 (d, *J* = 15.8 Hz, 1H), 1.30 (s, 18H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 153.2 (d, *J*(C,P) = 3.1 Hz), 149.6 (d, *J*(C,P) = 7.8 Hz), 136.1 (s), 136.0 (s), 135.7 (d, *J*(C,P) = 2.3 Hz), 135.7 (s), 133.2 (d, *J*(C,P) = 1.9 Hz), 133.0 (s), 131.9 (d, *J*(C,P) = 8.4 Hz), 131.2 (d, *J*(C,P) = 5.4 Hz), 130.7 (s), 128.7 (d, *J*(C,P) = 1.1 Hz), 127.8 (d, *J*(C,P) = 11.2 Hz), 126.6 (d, *J*(C,P) = 6.5 Hz), 125.7 (d, *J*(C,P) = 11.7 Hz), 125.2 (s), 124.7 (s), 124.4 (d, *J*(C,P) = 120.5 Hz), 123.9 (d, *J*(C,P) = 3.9 Hz), 123.6 (d, *J*(C,P) = 10.0 Hz), 122.7 (d, *J*(C,P) = 10.2 Hz), 120.7 (d, *J*(C,P) = 6.2 Hz), 50.0 (d, *J*(C,P) = 89.1 Hz), 34.2 (s), 30.1 (s); $^{31}P\{^1H\}$ NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 34.8. HRMS (ESI) *m/z*: calcd. for $C_{33}H_{35}BrO_3P$ $[M+H]^+$: 589.1507, found: 589.1504.

(Sp+Rc/Rp+Sc)-6-((2-bromophenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)-6H-dibenzo[c,e][1,2]oxaphosphinine 6-oxide (5g'). According to the general procedure, work-up and flash column chromatography (R_f = 0.4, hexane/EtOAc: 5:1) gave product **5g'** (56.4 mg, 0.10 mmol, 48%) as a colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C, TMS): δ = 8.30-8.33 (m, 1H), 7.83-7.86 (m, 2H), 7.58-7.64 (m, 2H), 7.32-7.42 (m, 4H), 7.20-7.24 (m, 1H), 7.02-7.09 (m, 4H), 5.08 (s, 1H), 5.03 (d, *J* = 15.8 Hz, 1H), 1.31 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$, 25 °C, TMS): δ = 153.1 (d, *J*(C,P) = 2.8 Hz), 150.0 (d, *J*(C,P) = 8.5 Hz), 136.5 (d, *J*(C,P) = 6.9 Hz), 135.6 (d, *J*(C,P) = 2.0 Hz), 135.4 (s), 133.3 (d, *J*(C,P) = 2.2 Hz), 133.1 (s), 131.4 (d, *J*(C,P) = 8.7 Hz), 131.1 (d, *J*(C,P) = 5.4 Hz)), 130.5 (s), 128.8 (d, *J*(C,P) = 1.7 Hz), 128.2 (d, *J*(C,P) = 12.6 Hz), 127.7 (d, *J*(C,P) = 1.5 Hz), 126.6 (d, *J*(C,P) = 6.2 Hz), 126.3 (d, *J*(C,P) = 12.1 Hz), 125.1 (s), 124.5 (s), 124.2 (d, *J*(C,P) = 118.3 Hz), 124.1 (d, *J*(C,P) = 7.4 Hz), 123.4 (d, *J*(C,P) = 9.8 Hz), 122.6 (d, *J*(C,P) = 10.0 Hz), 120.4 (d, *J*(C,P) = 6.5 Hz), 50.8 (d, *J*(C,P) = 89.8 Hz), 34.2 (s), 30.1 (s); ^{31}P{^{1}H} NMR (160 MHz, CDCl$_3$, 25 °C, TMS): δ = 33.5. HRMS (ESI) *m/z*: calcd. for $C_{33}H_{35}BrO_3P$ [M+H]$^+$: 589.1507, found: 589.1502.

*(Rp+Rc/Sp+Sc)-4-((3,5-di-tert-butyl-4-hydroxyphenyl)(6-oxido-6H-dibenzo[c,e][1,2]oxaphosphinin-6-yl)methyl)benzonitrile (**5h**).* According to the general procedure, work-up and flash column chromatography (R_f = 0.5, hexane/EtOAc: 1:1) gave product **5h** (39.5 mg, 0.07 mmol, 37%) as a colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C, TMS): δ = 7.88-7.92 (m, 2H), 7.61-7.69 (m, 5H), 7.23-7.37 (m, 4H), 6.96-6.98 (m, 1H), 6.90-6.91 (m, 2H), 5.16 (s, 1H), 4.36 (d, *J* = 17.8 Hz, 1H), 1.29 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$, 25 °C, TMS): δ = 153.5 (d, *J*(C,P) = 3.1 Hz), 149.7 (d, *J*(C,P) = 8.4 Hz), 141.4 (d, *J*(C,P) = 5.8 Hz), 136.1 (d, *J*(C,P) = 2.0 Hz), 133.6 (d, *J*(C,P) = 2.2 Hz), 132.3 (d, *J*(C,P) = 1.1 Hz), 132.0 (d, *J*(C,P) = 8.6 Hz), 130.8 (s), 130.4 (d, *J*(C,P) = 6.9 Hz), 128.1 (d, *J*(C,P) = 12.6 Hz), 126.6 (d, *J*(C,P) = 6.7 Hz), 125.2 (s), 124.7 (s), 123.5 (d, *J*(C,P) = 3.9 Hz), 123.4 (s), 123.3 (d, *J*(C,P) = 119.6 Hz), 122.2 (d, *J*(C,P) = 10.2 Hz), 120.2 (d, *J*(C,P) = 6.4 Hz), 118.9 (d, *J*(C,P) = 0.8 Hz), 111.1 (d, *J*(C,P) = 2.0 Hz), 52.7 (d, *J*(C,P) = 87.0 Hz), 34.3 (s), 30.1 (s); ^{31}P{^{1}H} NMR (160 MHz, CDCl$_3$, 25 °C, TMS): δ = 33.2. HRMS (ESI) *m/z*: calcd. for $C_{34}H_{35}NO_3P$ [M+H]$^+$: 536.2355, found: 536.2351.

*(Sp+Rc/Rp+Sc)-4-((3,5-di-tert-butyl-4-hydroxyphenyl)(6-oxido-6H-dibenzo[c,e][1,2]oxaphosphinin-6-yl)methyl)benzonitrile (**5h'**)*. According to the general procedure, work-up and flash column chromatography (R_f = 0.4, hexane/EtOAc: 1:1) gave product **5h'** (43.8 mg, 0.08 mmol, 41%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.85-7.88 (m, 1H), 7.80-7.82 (m, 1H), 7.64-7.70 (m, 4H), 7.59-7.61 (m, 2H), 7.39-7.43 (m, 1H), 7.32-7.36 (m, 1H), 7.19-7.23 (m, 1H), 6.99-7.02 (m, 1H), 6.88-6.89 (m, 2H), 5.13 (s, 1H), 4.43 (d, *J* = 15.3 Hz, 1H), 1.27 (s, 18H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 153.3 (d, *J*(C,P) = 3.1 Hz), 150.0 (d, *J*(C,P) = 8.8 Hz), 141.4 (d, *J*(C,P) = 3.3 Hz), 135.8 (d, *J*(C,P) = 2.2 Hz), 133.7 (d, *J*(C,P) = 2.2 Hz), 132.4 (s), 131.4 (d, *J*(C,P) = 9.1 Hz), 130.7 (s), 130.6 (d, *J*(C,P) = 2.9 Hz), 128.4 (d, *J*(C,P) = 12.8 Hz), 126.2 (d, *J*(C,P) = 6.0 Hz), 125.0 (s), 124.6 (s), 123.8 (d, *J*(C,P) = 7.2 Hz), 123.5 (d, *J*(C,P) = 10.0 Hz), 123.3 (d, *J*(C,P) = 118.4 Hz), 121.8 (d, *J*(C,P) = 10.0 Hz), 120.2 (d, *J*(C,P) = 6.6 Hz), 118.8 (s), 111.2 (d, *J*(C,P) = 1.8 Hz), 53.6 (d, *J*(C,P) = 88.4 Hz), 34.3 (s), 30.0 (s); $^{31}P\{^1H\}$ NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 32.7. HRMS (ESI) *m*/*z*: calcd. for $C_{34}H_{35}NO_3P$ $[M+H]^+$: 536.2355, found: 536.2349.

*(Rp+Rc/Sp+Sc)-6-((3,5-di-tert-butyl-4-hydroxyphenyl)(2,5-dimethoxyphenyl)methyl)-6H-dibenzo[c,e][1,2]oxaphosphinine 6-oxide (**5i**)*. According to the general procedure, work-up and flash column chromatography (R_f = 0.5, hexane/EtOAc: 5:1) gave product **5i** (54.7 mg, 0.10 mmol, 48%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.83-7.87 (m, 2H), 7.50-7.63 (m, 3H), 7.27-7.34 (m, 2H), 7.16-7.20 (m, 1H), 7.09-7.10 (m, 2H), 6.93-6.96 (m, 1H), 6.70-6.73 (m, 1H), 6.64-6.66 (m, 1H), 5.07 (s, 1H), 5.04 (d, *J* = 17.0 Hz, 1H), 3.75 (s, 3H), 3.44 (s, 3H), 1.32 (s, 18H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 153.3 (d, *J*(C,P) = 2.2 Hz), 153.0 (d, *J*(C,P) = 3.0 Hz), 150.8 (d, *J*(C,P) = 8.0 Hz), 150.3 (d, *J*(C,P) = 8.3 Hz), 136.1 (d, *J*(C,P) = 6.7 Hz), 135.6 (d, *J*(C,P) = 2.0 Hz), 132.9 (d, *J*(C,P) = 2.1 Hz), 132.0 (d, *J*(C,P) = 8.8 Hz), 130.2 (s), 127.7 (d, *J*(C,P) = 12.5 Hz), 126.7 (d, *J*(C,P) = 6.8 Hz), 125.0 (d, *J*(C,P) = 4.1 Hz), 124.9 (s), 124.8 (d, *J*(C,P) = 5.5 Hz), 124.6 (d, *J*(C,P) = 117.3 Hz), 124.1 (s), 123.2 (d, *J*(C,P) = 9.9 Hz), 122.4 (d, *J*(C,P) = 10.0 Hz), 120.3 (d, *J*(C,P) = 6.3 Hz), 115.8 (d, *J*(C,P) = 5.5 Hz), 113.9 (d, *J*(C,P) = 2.2 Hz), 111.5 (d, *J*(C,P) = 1.1 Hz), 55.8 (s), 55.6 (s), 43.7 (d, *J*(C,P) = 90.0 Hz), 34.3 (s), 30.2 (s); $^{31}P\{^1H\}$ NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 35.0. HRMS (ESI) *m*/*z*: calcd. for $C_{35}H_{40}O_5P$ $[M+H]^+$: 571.2613, found: 571.2609.

*(Sp+Rc/Rp+Sc)-6-((3,5-di-tert-butyl-4-hydroxyphenyl)(2,5-dimethoxyphenyl)methyl)-6H-dibenzo[c,e][1,2]oxaphosphinine 6-oxide (**5i'**).* According to the general procedure, work-up and flash column chromatography ($R_f = 0.4$, hexane/EtOAc: 2:1) gave product **5i'** (45.6 mg, 0.08 mmol, 39%) as a colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$, 25 ^{o}C, TMS): δ = 7.79-7.84 (m, 2H), 7.59-7.66 (m, 3H), 7.26-7.36 (m, 2H), 7.16-7.20 (m, 1H), 7.08-7.09 (m, 2H), 6.99-7.03 (m, 1H), 6.70-6.73 (m, 1H), 6.56-6.59 (m, 1H), 5.05 (s, 1H), 5.04 (d, *J* = 16.8 Hz, 1H), 3.83 (s, 3H), 3.36 (s, 3H), 1.31 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$, 25 ^{o}C, TMS): δ = 153.4 (d, *J*(C,P) = 2.3 Hz), 152.9 (d, *J*(C,P) = 2.9 Hz), 151.1 (d, *J*(C,P) = 8.4 Hz), 150.2 (d, *J*(C,P) = 8.5 Hz), 136.4 (d, *J*(C,P) = 6.6 Hz), 135.4 (d, *J*(C,P) = 2.1 Hz), 132.9 (d, *J*(C,P) = 2.2 Hz), 131.5 (d, *J*(C,P) = 8.9 Hz), 130.2 (s), 127.9 (d, *J*(C,P) = 12.5 Hz), 126.7 (d, *J*(C,P) = 6.4 Hz), 124.9 (d, *J*(C,P) = 5.4 Hz), 124.8 (s), 124.6 (d, *J*(C,P) = 117.3 Hz), 124.2 (s), 123.1 (s), 123.0 (s), 122.5 (d, *J*(C,P) = 10.0 Hz), 120.2 (d, *J*(C,P) = 6.4 Hz), 115.9 (d, *J*(C,P) = 5.5 Hz), 113.9 (d, *J*(C,P) = 2.5 Hz), 112.0 (d, *J*(C,P) = 1.3 Hz), 55.9 (s), 55.8 (s), 44.0 (d, *J*(C,P) = 89.7 Hz), 34.2 (s), 30.2 (s); ^{31}P{^{1}H} NMR (160 MHz, CDCl$_3$, 25 ^{o}C, TMS): δ = 34.6. HRMS (ESI) *m/z*: calcd. for $C_{35}H_{40}O_5P$ [M+H]$^+$: 571.2613, found: 571.2605.

*(Rp+Rc/Sp+Sc)-6-((3,5-di-tert-butyl-4-hydroxyphenyl)(4-hydroxy-3-methoxyphenyl)methyl)-6H-dibenzo[c,e][1,2]oxaphosphinine 6-oxide (**5j**).* According to the general procedure, work-up and flash column chromatography ($R_f = 0.5$, hexane/EtOAc: 1:1) gave product **5j** (37.2 mg, 0.07 mmol, 33%) as a colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$, 25 ^{o}C, TMS): δ = 7.85-7.90 (m, 2H), 7.60-7.64 (m, 1H), 7.36-7.41 (m, 1H), 7.26-7.30 (m, 2H), 7.18-7.21 (m, 2H), 6.94-6.99 (m, 3H), 6.81-6.86 (m, 2H), 5.79 (s, 1H), 5.08 (s, 1H), 4.26 (d, *J* = 18.3 Hz, 1H), 3.85 (s, 3H), 1.28 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$, 25 ^{o}C, TMS): δ = 153.1 (d, *J*(C,P) = 3.2 Hz), 150.1 (d, *J*(C,P) = 8.3 Hz), 146.4 (d, *J*(C,P) = 1.3 Hz), 144.9 (d, *J*(C,P) = 2.1 Hz), 136.1 (d, *J*(C,P) = 6.8 Hz), 135.6 (d, *J*(C,P) = 2.2 Hz), 133.2 (d, *J*(C,P) = 1.8 Hz), 132.1 (d, *J*(C,P) = 8.5 Hz), 130.5 (s), 127.9 (d, *J*(C,P) = 12.2 Hz), 127.1 (d, *J*(C,P) = 5.9 Hz), 126.5 (d, *J*(C,P) = 6.7 Hz), 125.0 (s), 124.8 (d, *J*(C,P) = 3.7 Hz), 124.3 (s), 124.0 (d, *J*(C,P) = 116.7 Hz), 123.3 (d, *J*(C,P) = 10.0 Hz), 122.6 (d, *J*(C,P) = 7.8 Hz), 122.4 (d, *J*(C,P) = 10.1 Hz), 120.4 (d, *J*(C,P) = 6.2 Hz), 114.4 (s), 112.2 (d, *J*(C,P) = 6.1 Hz), 55.8 (s), 52.3 (d, *J*(C,P) = 87.8 Hz), 34.2 (s), 30.1 (s); ^{31}P{^{1}H}

NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 34.5. HRMS (ESI) *m/z*: calcd. for $C_{34}H_{38}O_5P$ $[M+H]^+$: 557.2457, found: 557.2450.

*(Sp+Rc/Rp+Sc)-6-((3,5-di-tert-butyl-4-hydroxyphenyl)(4-hydroxy-3-methoxyphenyl)methyl)-6H-dibenzo[c,e][1,2]oxaphosphinine 6-oxide (**5j'**).* According to the general procedure, work-up and flash column chromatography (R_f = 0.4, hexane/EtOAc: 1:1) gave product **5j'** (48.8 mg, 0.09 mmol, 44%) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.80-7.85 (m, 2H), 7.59-7.68 (m, 2H), 7.31-7.39 (m, 2H), 7.18-7.21 (m, 1H), 7.09-7.10 (m, 1H), 7.00-7.03 (m, 3H), 6.93-6.95 (m, 1H), 6.79-6.80 (m, 1H), 5.78 (s, 1H), 5.08 (s, 1H), 4.26 (d, *J* = 16.0 Hz, 1H), 3.85 (s, 3H), 1.30 (s, 18H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 153.0 (d, *J*(C,P) = 3.1 Hz), 150.1 (d, *J*(C,P) = 8.5 Hz), 146.5 (s), 145.0 (d, *J*(C,P) = 2.1 Hz), 136.1 (d, *J*(C,P) = 6.5 Hz), 135.5 (d, *J*(C,P) = 2.4 Hz), 133.2 (s), 131.2 (d, *J*(C,P) = 8.9 Hz), 130.4 (s), 128.2 (d, *J*(C,P) = 12.6 Hz), 127.0 (d, *J*(C,P) = 3.4 Hz), 126.2 (d, *J*(C,P) = 6.0 Hz), 125.1 (d, *J*(C,P) = 7.1 Hz), 125.0 (s), 124.3 (s), 124.0 (d, *J*(C,P) = 116.4 Hz), 123.3 (d, *J*(C,P) = 9.9 Hz), 123.0 (d, *J*(C,P) = 8.3 Hz), 122.3 (d, *J*(C,P) = 6.5 Hz), 120.3 (d, *J*(C,P) = 6.5 Hz), 114.5 (s), 112.5 (d, *J*(C,P) = 7.9 Hz), 55.9 (s), 52.9 (d, *J*(C,P) = 88.5 Hz), 34.3 (s), 30.1 (s); $^{31}P\{^1H\}$ NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 33.9. HRMS (ESI) *m/z*: calcd. for $C_{34}H_{38}O_5P$ $[M+H]^+$: 557.2457, found: 557.2452.

*(Rp+Rc/Sp+Sc, Sp+Rc/Rp+Sc)-methyl ((3,5-di-tert-butyl-4-hydroxyphenyl)(phenyl)methyl)(phenyl) phosphinate (**5k+5k'**).* According to the general procedure, work-up and flash column chromatography (R_f = 0.4, hexane/EtOAc: 2:1) gave product **5k+5k'** (82.8 mg, 0.18 mmol, 92%) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.60-7.62 (m, 1H), 7.48-7.53 (m, 2H), 7.27-7.45 (m, 6H), 7.11-7.24 (m, 2H), 7.00-7.01 (m, 1H), 5.04-5.13 (s, 1H), 4.34-4.41 (d, *J* = 4.8 Hz, 4.4 Hz, 1H), 3.55-3.58 (d, *J* = 3.2 Hz, 3.2 Hz, 3H), 1.29-1.40 (s, 18H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 153.0 (d, *J*(C,P) = 2.4 Hz), 152.7 (d, *J*(C,P) = 2.9 Hz), 137.2 (d, *J*(C,P) = 6.3 Hz), 136.8 (d, *J*(C,P) =2.7 Hz), 135.7 (d, *J*(C,P) = 1.5 Hz), 135.5 (d, *J*(C,P) = 2.1 Hz), 132.3 (d, *J*(C,P) = 1.9 Hz), 132.2 (d, *J*(C,P) = 2.0 Hz), 131.9 (d, *J*(C,P) = 2.7 Hz), 131.8 (d, *J*(C,P) = 2.6 Hz), 130.2 (d, *J*(C,P) = 125.1 Hz), 130.1 (d, *J*(C,P) = 124.3 Hz), 129.8 (d, *J*(C,P) = 7.1 Hz), 129.7 (d, *J*(C,P) = 7.1 Hz), 128.5 (d, *J*(C,P) = 0.6 Hz), 128.4 (d, *J*(C,P) = 1.4 Hz), 128.1 (d, *J*(C,P) = 2.6 Hz), 128.0 (d, *J*(C,P) = 2.6 Hz), 127.0 (d,

J(C,P) = 1.7 Hz), 126.8 (d, *J*(C,P) = 1.2 Hz), 126.7 (d, *J*(C,P) = 2.5 Hz), 126.6 (s), 126.5 (d, *J*(C,P) = 2.3 Hz), 126.2 (d, *J*(C,P) = 3.5 Hz), 54.4 (d, *J*(C,P) = 93.6 Hz), 54.2 (d, *J*(C,P) = 94.1 Hz), 51.9 (s), 51.8 (s), 34.4 (s), 34.2 (s), 30.3 (s), 30.2 (s); ^{31}P{^{1}H} NMR (160 MHz, CDCl$_3$, 25 °C, TMS): δ = 41.6 (44%), 42.6 (48%). HRMS (ESI) *m*/*z*: calcd. for $C_{28}H_{34}O_3P$ [M-H]$^-$: 449.2246, found: 449.2241.

*(Rp+Rc/Sp+Sc, Sp+Rc/Rp+Sc)-ethyl ((3,5-di-tert-butyl-4-hydroxyphenyl)(phenyl)methyl)(phenyl) phosphinate (**5l+5l'**).* According to the general procedure, work-up and flash column chromatography (R$_f$ = 0.4, hexane/EtOAc: 2:1) gave product **5l+5l'** (83.5 mg, 0.18 mmol, 90%) as a colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C, TMS): δ = 7.57-7.62 (m, 1H), 7.39-7.52 (m, 4H), 7.27-7.34 (m, 3H), 7.13-7.24 (m, 3H), 7.00-7.05 (m, 1H), 5.04-5.12 (s, 1H), 4.33-4.38 (d, *J* = 4.8 Hz, 4.7 Hz, 1H), 3.80-4.02 (m, 2H), 1.30-1.39 (s, 18H), 1.16-1.21 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$, 25 °C, TMS): δ = 152.8 (d, *J*(C,P) = 16.7 Hz), 137.4 (d, *J*(C,P) = 6.0 Hz), 136.8 (d, *J*(C,P) = 2.7 Hz), 135.6 (d, *J*(C,P) =1.7 Hz), 135.5 (d, *J*(C,P) = 2.0 Hz), 132.2 (d, *J*(C,P) = 6.4 Hz), 132.1 (d, *J*(C,P) = 6.5 Hz), 131.8 (d, *J*(C,P) = 2.6 Hz), 131.7 (d, *J*(C,P) = 2.9 Hz), 131.1 (d, *J*(C,P) = 126.3 Hz), 130.9 (d, *J*(C,P) = 124.3 Hz), 129.9 (d, *J*(C,P) = 6.8 Hz), 129.7 (d, *J*(C,P) = 7.1 Hz), 128.4 (d, *J*(C,P) = 0.6 Hz), 128.3 (d, *J*(C,P) = 1.3 Hz), 128.0 (d, *J*(C,P) = 5.5 Hz), 127.9 (d, *J*(C,P) = 5.6 Hz), 126.9 (d, *J*(C,P) = 1.3 Hz), 126.8 (d, *J*(C,P) = 2.3 Hz), 126.7 (s), 126.6 (s), 126.6 (s), 126.5 (s), 126.4 (d, *J*(C,P) = 3.0 Hz), 61.3 (d, *J*(C,P) = 7.0 Hz), 61.2 (d, *J*(C,P) = 6.9 Hz), 54.1 (d, *J*(C,P) = 93.2 Hz), 54.5 (d, *J*(C,P) = 93.6 Hz), 34.4 (s), 34.2 (s), 30.3 (s), 30.2 (s), 16.5 (s), 16.4 (s); ^{31}P{^{1}H} NMR (160 MHz, CDCl$_3$, 25 °C, TMS): δ = 40.4 (48%), 39.8 (52%). HRMS (ESI) *m*/*z*: calcd. for $C_{29}H_{36}O_3P$ [M-H]$^-$: 463.2402, found: 463.2398.

*(Rp+Rc/Sp+Sc, Sp+Rc/Rp+Sc)-ethyl ((3,5-di-tert-butyl-4-hydroxyphenyl)(o-tolyl)methyl)(phenyl) phosphinate (**5m+5m'**).* According to the general procedure, work-up and flash column chromatography (R$_f$ = 0.5, hexane/EtOAc: 2:1) gave product **5m+5m'** (85.1 mg, 0.18 mmol, 89%) as a colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C, TMS): δ = 8.03-8.09 (m, 1H), 7.38-7.56 (m, 3H), 7.09-7.32 (m, 5H), 6.95-7.06 (m, 2H), 5.05-5.13 (s, 1H), 4.56-4.60 (d, *J* = 4.3 Hz, 4.7 Hz, 1H), 3.78-4.02 (m, 2H), 2.12-2.26 (s, 3H), 1.29-1.39 (s, 18H), 1.15-1.21 (m, 3H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$, 25 °C, TMS): δ = 152.8 (d, *J*(C,P) = 1.7 Hz), 152.6 (d, *J*(C,P) = 2.9 Hz), 136.5 (s), 136.4 (d, *J*(C,P) =3.0 Hz), 136.3 (s), 136.1 (d, *J*(C,P) = 5.0 Hz), 135.5 (d, *J*(C,P) = 1.9 Hz), 135.4 (d, *J*(C,P) = 3.8 Hz), 135.4 (s), 132.1 (d,

J(C,P) = 8.9 Hz), 131.9 (d, *J*(C,P) = 9.2 Hz), 131.3 (d, *J*(C,P) = 118.5 Hz), 131.2 (d, *J*(C,P) = 109.2 Hz), 130.7 (d, *J*(C,P) = 6.4 Hz), 130.4 (d, *J*(C,P) = 6.1 Hz), 129.6 (d, *J*(C,P) = 5.3 Hz), 128.1 (d, *J*(C,P) = 3.9 Hz), 127.9 (d, *J*(C,P) = 3.9 Hz), 126.9 (s), 126.9 (s), 126.8 (s), 126.8 (s), 126.3 (d, *J*(C,P) = 7.3 Hz), 126.1 (d, *J*(C,P) = 1.3 Hz), 126.3 (d, *J*(C,P) = 1.6 Hz), 125.9 (d, *J*(C,P) = 3.5 Hz), 61.2 (d, *J*(C,P) = 6.9 Hz), 61.0 (d, *J*(C,P) = 6.8 Hz), 49.5 (d, *J*(C,P) = 95.3 Hz), 49.4 (d, *J*(C,P) = 95.1 Hz), 34.4 (s), 34.2 (s), 30.3 (s), 30.2 (s), 20.2 (s), 20.1 (s), 16.5 (s), 16.4 (s); $^{31}P\{^1H\}$ NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 41.2 (36%), 40.1 (53%). HRMS (ESI) *m/z*: calcd. for $C_{30}H_{38}O_3P$ $[M-H]^-$: 477.2559, found: 477.2556.

*(Rp+Rc/Sp+Sc, Sp+Rc/Rp+Sc)-ethyl((3,5-di-tert-butyl-4-hydroxyphenyl)(3-methoxyphenyl)methyl)(phenyl)phosphinate (**5n+5n'**).* According to the general procedure, work-up and flash column chromatography (R_f = 0.4, hexane/EtOAc: 2:1) gave product **5n+5n'** (83.1 mg, 0.17 mmol, 84%) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.46-7.53 (m, 2H), 7.39-7.43 (m, 1H), 7.27-7.31 (m, 2H), 7.11-7.24 (m, 3H), 6.99-7.05 (m, 2H), 6.70-6.81 (m, 1H), 5.06-5.14 (s, 1H), 4.31-4.35 (d, *J* = 4.5 Hz, 4.4 Hz, 1H), 3.82-4.02 (m, 2H), 3.72-3.79 (s, 3H), 1.31-1.39 (s, 18H), 1.17-1.22 (m, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 159.5 (d, *J*(C,P) = 0.5 Hz), 159.3 (d, *J*(C,P) = 1.1 Hz), 152.9 (d, *J*(C,P) = 2.4 Hz), 152.7 (d, *J*(C,P) =2.8 Hz), 138.7 (d, *J*(C,P) = 5.9 Hz), 138.3 (d, *J*(C,P) = 2.7 Hz), 135.6 (d, *J*(C,P) = 1.6 Hz), 135.5 (d, *J*(C,P) = 2.0 Hz), 132.2 (d, *J*(C,P) = 9.0 Hz), 132.1 (d, *J*(C,P) = 9.1 Hz), 131.7 (d, *J*(C,P) = 2.6 Hz), 131.7 (d, *J*(C,P) = 2.7 Hz), 131.0 (d, *J*(C,P) = 125.2 Hz), 130.9 (d, *J*(C,P) = 124.5 Hz), 129.3 (d, *J*(C,P) = 0.8 Hz), 129.2 (d, *J*(C,P) = 1.3 Hz), 128.0 (d, *J*(C,P) = 12.3 Hz), 127.9 (d, *J*(C,P) = 12.3 Hz), 126.7 (s), 126.6 (d, *J*(C,P) = 6.6 Hz), 126.5 (d, *J*(C,P) = 6.8 Hz), 126.3 (d, *J*(C,P) = 3.3 Hz), 122.3 (s), 122.3 (s), 122.2 (s), 115.1 (d, *J*(C,P) = 7.2 Hz), 115.0 (d, *J*(C,P) = 7.4 Hz), 61.3 (d, *J*(C,P) = 6.9 Hz), 61.1 (d, *J*(C,P) = 6.9 Hz), 55.2 (s), 55.1 (s), 54.6 (d, *J*(C,P) = 93.1 Hz), 54.5 (d, *J*(C,P) = 93.4 Hz), 34.4 (s), 34.3 (s), 30.3 (s), 30.2 (s), 20.2 (s), 20.1 (s), 16.5 (d, *J*(C,P) = 5.9 Hz), 16.5 (d, *J*(C,P) = 6.3 Hz); $^{31}P\{^1H\}$ NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 40.3 (35%), 39.7 (49%). HRMS (ESI) *m/z*: calcd. for $C_{30}H_{38}O_4P$ $[M-H]^-$: 493.2508, found: 493.2503.

*(Rp+Rc/Sp+Sc)-ethyl ((3,5-di-tert-butyl-4-hydroxyphenyl)(3-nitrophenyl)methyl)(phenyl)phosphinate (**5o**).* According to the general procedure, work-up and flash column chromatography (R_f = 0.5, hexane/EtOAc: 2:1) gave product **5o** (38.3 mg, 0.08 mmol, 39%) as a colorless oil. ^1H NMR (400 MHz,

$CDCl_3$, 25 °C, TMS): δ = 8.39-8.40 (m, 1H), 8.05-8.14 (m, 2H), 7.43-7.54 (m, 4H), 7.30-7.35 (m, 2H), 7.02-7.03 (m, 2H), 5.11 (s, 1H), 4.46 (d, *J* = 18.2 Hz, 1H), 3.85-4.08 (m, 2H), 1.31 (s, 18H), 1.21 (t, *J*(C,P) = 7.0 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 153.1 (d, *J*(C,P) = 2.7 Hz), 148.2 (s), 139.5 (d, *J*(C,P) = 6.3 Hz), 135.9 (d, *J*(C,P) =1.8 Hz), 135.7 (d, *J*(C,P) = 5.9 Hz), 132.2 (s), 132.1 (d, *J*(C,P) = 3.3 Hz), 130.1 (d, *J*(C,P) = 126.6 Hz), 129.3 (d, *J*(C,P) = 1.3 Hz), 128.1 (d, *J*(C,P) = 12.5 Hz), 126.6 (d, *J*(C,P) = 7.6 Hz), 125.0 (s), 124.9 (d, *J*(C,P) = 2.8 Hz), 121.9 (d, *J*(C,P) = 1.4 Hz), 61.5 (d, *J*(C,P) = 6.8 Hz), 53.7 (d, *J*(C,P) = 93.7 Hz), 34.3 (s), 30.1 (s), 16.5 (d, *J*(C,P) = 6.0 Hz); $^{31}P\{^1H\}$ NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 39.7 (s). HRMS (ESI) *m/z*: calcd. for $C_{29}H_{35}NO_5P$ $[M-H]^-$: 508.2253, found: 508.2250.

*(Sp+Rc/Rp+Sc)-ethyl ((3,5-di-tert-butyl-4-hydroxyphenyl)(3-nitrophenyl)methyl)(phenyl)phosphinate **(5o')***. According to the general procedure, work-up and flash column chromatography (R_f = 0.4, hexane/EtOAc: 2:1) gave product **5o'** (43.9 mg, 0.09 mmol, 46%) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.21-8.22 (m, 1H), 8.04-8.06 (m, 1H), 7.91-7.93 (m, 1H), 7.42-7.50 (m, 4H), 7.30-7.35 (m, 2H), 7.20-7.21 (m, 2H), 5.19 (s, 1H), 4.45 (d, *J* = 18.3 Hz, 1H), 3.84-4.06 (m, 2H), 1.39 (s, 18H), 1.23 (t, *J*(C,P) = 7.0 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 153.3 (d, *J*(C,P) = 2.4 Hz), 148.0 (s), 139.2 (d, *J*(C,P) = 2.9 Hz), 136.0 (d, *J*(C,P) = 1.6 Hz), 135.9 (d, *J*(C,P) =6.3 Hz), 132.3 (d, *J*(C,P) = 2.7 Hz), 132.1 (d, *J*(C,P) = 9.2 Hz), 123.0 (d, *J*(C,P) = 125.8 Hz), 129.3 (d, *J*(C,P) = 1.4 Hz), 128.3 (d, *J*(C,P) = 12.4 Hz), 126.6 (d, *J*(C,P) = 6.3 Hz), 125.6 (d, *J*(C,P) = 6.4 Hz), 124.7 (d, *J*(C,P) = 7.7 Hz), 121.9 (d, *J*(C,P) = 2.0 Hz), 61.6 (d, *J*(C,P) = 6.8 Hz), 54.3 (d, *J*(C,P) = 93.0 Hz), 34.4 (s), 30.2 (s), 16.4 (d, *J*(C,P) = 6.3 Hz); $^{31}P\{^1H\}$ NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 38.7 (s). HRMS (ESI) *m/z*: calcd. for $C_{29}H_{35}NO_5P$ $[M-H]^-$: 508.2253, found: 508.2247.

*(Rp+Rc/Sp+Sc,Sp+Rc/Rp+Sc)-ethyl((3,5-di-tert-butyl-4-hydroxyphenyl)(5-methylfuran-2-yl)methyl)(phenyl)phosphinate **(5p+5p')***. According to the general procedure, work-up and flash column chromatography (R_f = 0.5, hexane/EtOAc: 2:1) gave product **5p+5p'** (75.8 mg, 0.16 mmol, 81%) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.38-7.51 (m, 3H), 7.26-7.35 (m, 2H), 6.94-7.05 (m, 2H), 6.29-6.37 (m, 1H), 5.87-5.92 (m, 1H), 5.08-5.13 (s, 1H), 4.46-4.47 (d, *J* = 5.2 Hz, 5.2 Hz, 1H), 3.84-4.15 (m, 2H), 2.19-2.23 (s, 3H), 1.31-1.35 (s, 18H), 1.21-1.28 (m, 3H); $^{13}C\{^1H\}$ NMR (100

MHz, $CDCl_3$, 25 °C, TMS): δ = 153.1 (d, *J*(C,P) = 3.1 Hz), 152.9 (d, *J*(C,P) = 3.4 Hz), 151.3 (d, *J*(C,P) = 2.5 Hz), 151.2 (d, *J*(C,P) =2.0 Hz), 147.9 (d, *J*(C,P) = 3.8 Hz), 147.8 (d, *J*(C,P) = 2.5 Hz), 135.5 (d, *J*(C,P) = 2.5 Hz), 135.4 (d, *J*(C,P) = 2.6 Hz), 132.4 (d, *J*(C,P) = 6.2 Hz), 132.3 (d, *J*(C,P) = 6.2 Hz), 131.9 (d, *J*(C,P) = 2.7 Hz), 131.8 (d, *J*(C,P) = 2.8 Hz), 130.2 (d, *J*(C,P) = 126.5 Hz), 130.1 (d, *J*(C,P) = 127.0 Hz), 127.9 (d, *J*(C,P) = 7.9 Hz), 127.8 (d, *J*(C,P) = 7.9 Hz), 126.6 (d, *J*(C,P) = 5.2 Hz), 126.5 (d, *J*(C,P) = 5.3 Hz), 124.5 (d, *J*(C,P) = 5.8 Hz), 124.4 (d, *J*(C,P) = 4.1 Hz), 109.6 (d, *J*(C,P) = 5.5 Hz), 109.5 (d, *J*(C,P) = 5.2 Hz), 106.6 (d, *J*(C,P) = 1.6 Hz), 106.5 (d, *J*(C,P) = 1.8 Hz), 61.4 (d, *J*(C,P) = 7.0 Hz), 61.2 (d, *J*(C,P) = 6.9 Hz), 48.7 (d, *J*(C,P) = 93.7 Hz), 48.6 (d, *J*(C,P) = 93.9 Hz), 34.3 (s), 34.2 (s), 30.2 (s), 30.1 (s), 16.5 (d, *J*(C,P) = 6.2 Hz), 16.4 (d, *J*(C,P) = 6.5 Hz), 13.6 (s), 13.5 (s); $^{31}P\{^1H\}$ NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 38.0 (37%), 37.3 (44%). HRMS (ESI) *m/z*: calcd. for $C_{28}H_{38}O_4P$ $[M+H]^+$: 469.2508, found: 469.2505.

*(Rp+Rc/Sp+Sc)-ethyl ((3,5-di-tert-butyl-4-hydroxyphenyl)(thiophen-2-yl)methyl)(phenyl)phosphinate (**5q**)*. According to the general procedure, work-up and flash column chromatography (R_f = 0.5, hexane/EtOAc: 2:1) gave product **5q** (38.5 mg, 0.08 mmol, 41%) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.40-7.45 (m, 3H), 7.26-7.30 (m, 2H), 7.20-7.22 (m, 2H), 7.02-7.03 (m, 2H), 6.96-6.99 (m, 1H), 5.08 (s, 1H), 4.59 (d, *J* = 19.3 Hz, 1H), 3.89-4.13 (m, 2H), 1.31 (s, 18H), 1.26 (t, *J*(C,P) = 6.8 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 153.0 (d, *J*(C,P) = 3.2 Hz), 138.9 (d, *J*(C,P) = 6.5 Hz), 135.5 (d, *J*(C,P) = 2.3 Hz), 132.3 (d, *J*(C,P) = 9.1 Hz), 131.8 (d, *J*(C,P) = 2.7 Hz), 130.2 (d, *J*(C,P) = 126.4 Hz), 127.9 (d, *J*(C,P) = 12.5 Hz), 127.2 (d, *J*(C,P) = 6.8 Hz), 126.8 (d, *J*(C,P) = 2.3 Hz), 126.5 (d, *J*(C,P) = 6.0 Hz), 125.8 (d, *J*(C,P) = 3.6 Hz), 124.7 (d, *J*(C,P) = 2.4 Hz), 61.6 (d, *J*(C,P) = 7.0 Hz), 49.9 (d, *J*(C,P) = 93.8 Hz), 34.2 (s), 30.2 (s), 16.5 (d, *J*(C,P) = 6.0 Hz); $^{31}P\{^1H\}$ NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 38.7 (s). HRMS (ESI) *m/z*: calcd. for $C_{27}H_{36}O_3PS$ $[M+H]^+$: 471.2123, found: 471.2116.

*(Sp+Rc/Rp+Sc)-ethyl ((3,5-di-tert-butyl-4-hydroxyphenyl)(thiophen-2-yl)methyl)(phenyl)phosphinate (**5q'**)*. According to the general procedure, work-up and flash column chromatography (R_f = 0.4, hexane/EtOAc: 2:1) gave product **5q'** (38.8 mg, 0.08 mmol, 41%) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.42-7.49 (m, 3H), 7.28-7.33 (m, 2H), 7.12-7.15 (m, 4H), 6.91-6.93 (m,

1H), 5.14 (s, 1H), 4.63 (d, *J* = 19.6 Hz, 1H), 3.85-4.01 (m, 2H), 1.37 (s, 18H), 1.21 (t, *J*(C,P) = 7.0 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 153.1 (d, *J*(C,P) = 2.9 Hz), 138.9 (d, *J*(C,P) = 4.4 Hz), 135.6 (d, *J*(C,P) = 2.1 Hz), 132.3 (d, *J*(C,P) = 9.1 Hz), 131.9 (d, *J*(C,P) = 2.7 Hz), 130.2 (d, *J*(C,P) = 125.8 Hz), 128.0 (d, *J*(C,P) = 12.4 Hz), 127.3 (d, *J*(C,P) = 7.0 Hz), 126.7 (d, *J*(C,P) = 2.4Hz), 126.6 (d, *J*(C,P) = 5.7 Hz), 126.2 (d, *J*(C,P) = 6.0 Hz), 124.7 (d, *J*(C,P) = 2.7 Hz), 61.5 (d, *J*(C,P) = 7.0 Hz), 50.1 (d, *J*(C,P) = 93.8 Hz), 34.3 (s), 30.2 (s), 16.5 (d, *J*(C,P) = 6.4 Hz); $^{31}P\{^1H\}$ NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 37.9 (s). HRMS (ESI) *m*/*z*: calcd. for $C_{27}H_{36}O_3PS$ $[M+H]^+$: 471.2123, found: 471.2119.

*Diethyl ((3,5-di-tert-butyl-4-hydroxyphenyl)(phenyl)methyl)phosphonate (**3a'**).* According to the general procedure, work-up and flash column chromatography (R_f = 0.4, Hexane/EtOAc: 5:1) gave product **3a'** (82.1 mg, 0.19 mmol, 89%) as a colorless oil.[15b] ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.53-7.55 (m, 2H), 7.29-7.33 (m, 4H), 7.21-7.25 (m, 1H), 5.15 (s, 1H), 4.33 (d, *J* = 25.2 Hz, 0.8H), 3.75-4.00 (m, 4H), 1.41 (s, 18H), 1.01 (dt, *J* = 11.6, 7.1 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 152.9 (d, *J*(C,P) = 2.5 Hz), 137.4 (d, *J*(C,P) = 4.8 Hz), 135.8 (d, *J*(C,P) = 1.3 Hz), 129.5 (d, *J*(C,P) = 7.9 Hz), 128.5 (d, *J*(C,P) = 1.1 Hz), 127.0 (d, *J*(C,P) = 5.5 Hz), 126.9 (d, *J*(C,P) = 2.1 Hz), 126.2 (d, *J*(C,P) = 7.8 Hz), 62.5 (dd, ^1J(C,P) = 18.0 Hz, ^2J(C,P) = 7.0 Hz), 51.2 (d, *J*(C,P) = 136.6 Hz), 34.4 (s), 30.3 (s), 16.3 (t, *J*(C,P) = 6.1 Hz); $^{31}P\{^1H\}$ NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 25.9.

Supporting Information : The Supporting Information is available free of charge at http://pubs.acs.org.

Crystallographic data; ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$ and $^{19}F\{^1H\}$ NMR spectra (PDF); HRMS spectra;

FAIR data which includes primary NMR FID files for compounds **3a-3ae**, **3a'**, **4a-4s** and **5a-5q'** (ZIP)

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(18) CCDC 2053888 (for **5a**), and 2088472 (for **5a'**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.