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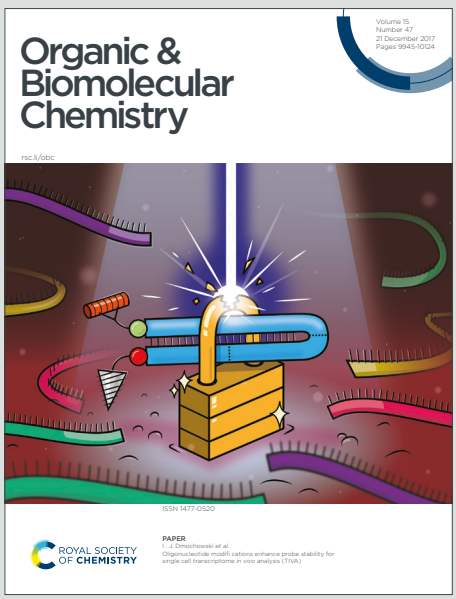

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ARTICLE

Microwave-assisted periselective annulation of triarylphosphenes with aldehydes and ketones

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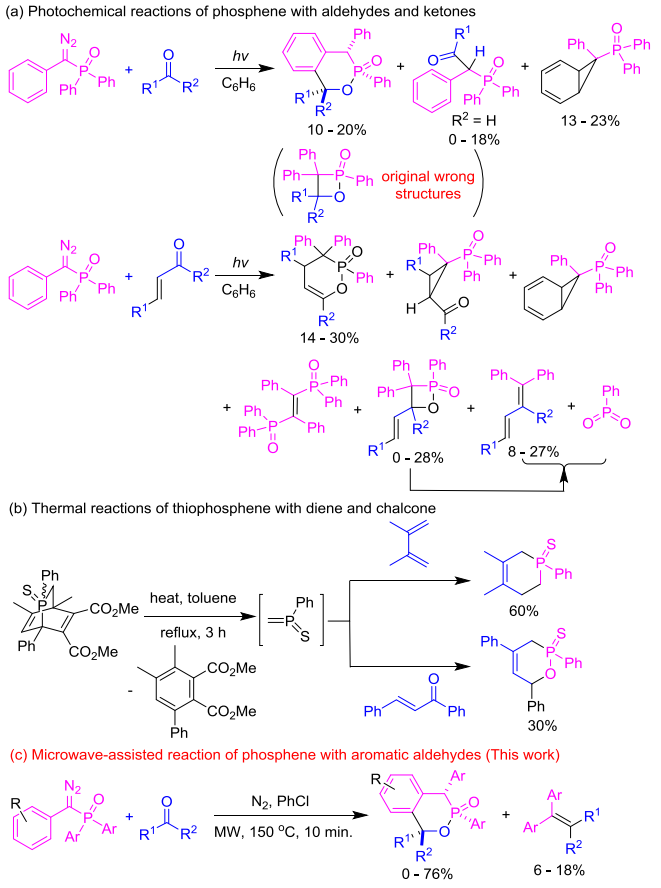
The reaction of (diazo(aryl)methyl)(diaryl)phosphine oxides with aldehydes and ketones generates benzo-δ-phospholactones in low to good yields with 1,1-diarylalk-1-enes as byproducts under microwave irradiation. (Diazo(aryl)methyl)(diaryl)phosphine oxides first undergo a Wolff rearrangement to form diaryl(aryl)phosphenes, which further react with aldehydes and ketones to afford benzo-δ-phospholactones and β-phospholactones. The latter are instable under heating and fragment into the corresponding 1,1-diarylalk-1-enes and arylphosphine dioxides under reaction conditions. The arylphosphine dioxides become arylphosphonic acids during workup. The periselectivity in the annulation shows that the reaction of diaryl(aryl)phosphenes with most aldehydes and ketones favors phosphene phenyl participating (4+2) annulation over (2+2) annulation.

Introduction

Phosphenes, the phosphorus analogues of ketenes, should be important intermediates and can be applied in some nucleophilic additions, annulations, and cycloadditions. However, compared with ketenes[1] and sulfenes,[2] only limited attentions have been paid previously to the annulation and cycloaddition of phosphenes.[3,4] The phosphenes have been prepared *in situ* previously via photo and thermal Wollf rearrangements of diazomethylphosphine oxide derivatives[3] and retro-Diels-Alder cycloadditions of 2-phosphabicyclo[2.2.2]octa-5,7-diene derivatives.[4]

Similar as active intermediate ketenes and sulfenes, phosphenes undergo nucleophilic addition with nucleophiles, such as water, alcohols, and amines,[3a,b,4a,c,d] and annulation or cycloaddition with unsaturated compounds, including aldehydes,[3b,e,6] ketones,[3c] unsaturated aldehydes and chalcones,[3e,f,4a] and 1,3-dienes (Scheme 1a,b).[4a] However, in the previous photochemical reactions of diazomethylphosphine oxide derivatives with aldehydes and ketones, besides (4+2) annulation products, both the carbene insertion products (for aldehydes) and the carbene cyclopropanation products (for solvent benzene and for the C=C double bond of unsaturated ketones) appear. Additionally, for the unsaturated ketones, the dimers of the carbenes, 4-(alk-1-enyl)-1,2-oxaphosphetane 2-oxides, and conjugated dienes generate as well (Scheme 1a). The thermal reactions of phenylthiophosphene with 2,3-dimethylbut-1,3-diene and chalcone give rise to [2+4] cycloaddition products, respectively (Scheme 1b). The annulated products benzo-δ-phospholactones were obtained in only very low yields in the previously reported methods from phosphenes.[3b-f,6] The benzo-δ-phospholactones are very useful



Scheme 1. Annulation of phosphenes and unsaturated bonds.

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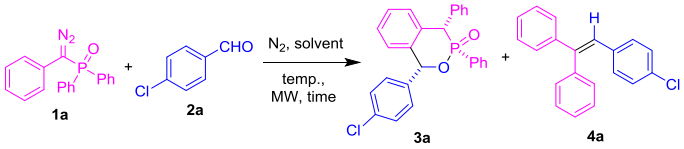
Electronic Supplementary Information (ESI) available: Copies of ^{1}H, ^{13}C, and ^{19}F NMR spectra of products **3** and **4**. See DOI: 10.1039/x0xx00000x

and important biological compounds.[7] Thus, an efficient synthetic method for the preparation of δ-phospholactones, especial benzo-δ-phospholactones, are in high demand. Herein, we report a microwave-assisted periselective synthesis of benzo-δ-phospholactones from (diazo)arylmethyl(diaryl)phosphine oxides with aldehydes and ketones in satisfactory yields in most cases (Scheme 1c).

Results and Discussion

It is well known that microwave can accelerate some organic reactions and improve the reaction selectivities and yields.[8] The microwave can promote the Wolff rearrangement of diazomethyl ketones to ketenes and the subsequent cycloaddition with imines.[9] Thus, we envisioned that microwave might improve the annulation of (diazo)arylmethyl(diaryl)phosphine oxides with aldehydes and ketones. We first selected the reaction of (diazo)phenylmethyl(diphenyl)phosphine oxide (**1a**) and 4-chlorobenzaldehyde (**2a**) as a model reaction to optimize the reaction conditions under the microwave irradiation. We started solvent evaluation at 130 °C. The results indicated that a slightly high yield was obtained in chlorobenzene as solvent for the desired benzo-δ-phospholactone **3a** (Table 1, entries 1–5). Further temperature screening was conducted in chlorobenzene, revealing that 150 °C was the best choice (Table 1, entries 5–12). Both decreasing and increasing amounts of aldehyde **2a** resulted in the lowering of the yield (Table 1, entries 13 and 14). Neither lengthening nor shortening the reaction time further improved the yield (Table 1, entries 15 and 16). Under classical oil-bath heating conditions, the reaction needed a long time but with a relatively low yield (Table 1, entry 17). In each of optimization reactions, byproduct 2-(4-chlorophenyl)-1,1-diphenylethene (**4a**) was obtained in low yields varied from 5–21%.

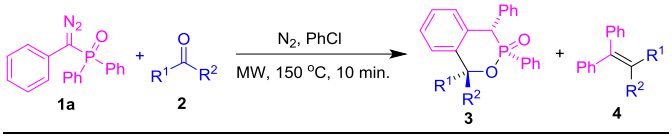
Table 1. Optimization on the Reaction Conditions[a]



entry	Solvent	Temp./ °C	Time/ min.	yield/%[b] **3a**	yield/%[b] **4a**
1	DCE	130	10	60	14
2	PhMe	130	10	60	6
3	MeCN	130	10	42	9
4	xylenes	130	10	53	10
5	PhCl	130	10	62	10
6	PhCl	100	80	51	12
7	PhCl	110	10	47	5
8	PhCl	130	20	58	14
9	PhCl	140	10	64	17
10	**PhCl**	**150**	**10**	**66**	**17**
11	PhCl	160	10	65	21
12	PhCl	170	10	65	16
13[c]	PhCl	150	10	52	19
14[d]	PhCl	150	10	59	10
15	PhCl	150	15	64	12
16	PhCl	150	3	58	14
17[e]	PhCl	150	120	54	12

[a]Reaction conditions: **1a** (0.2 mmol) and **2a** (0.8 mmol) in 3 mL of anhydrous solvent in a capped microwave reaction tube filled with N_2 were heated under microwave irradiation. [b]Yield of the isolated product. [c]**2a** (0.4 mmol). [d]**2a** (1.0 mmol). [e]Under classical oil-bath heating.

Table 2. Scope of Aldehydes and Ketones.[a]



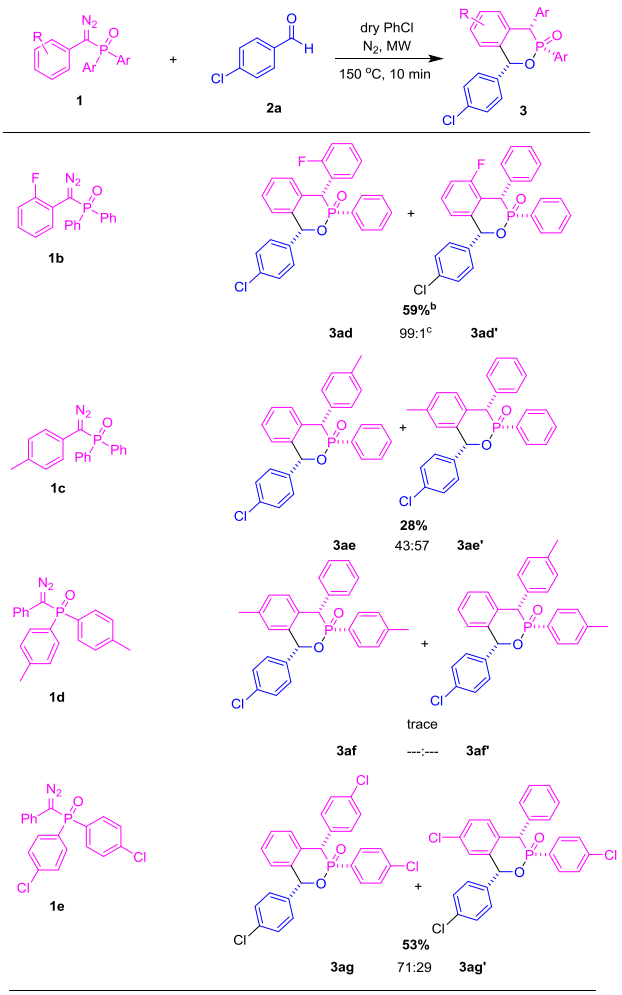
entry	**2**	R^1	R^2	yield/%[b] **3**	yield/%[b] **4**
1	**2a**	4-ClC_6H_4	H	66	17
2	**2b**	4-BrC_6H_4	H	60	18
3	**2c**	4-FC_6H_4	H	55	7
4	**2d**	4-MeC_6H_4	H	63	7
5	**2e**	4-*i*PrC_6H_4	H	65	12
6	**2f**	4-$MeOC_6H_4$	H	47	7
7	**2g**	4-NCC_6H_4	H	48	18
8	**2h**	4-$O_2NC_6H_4$	H	46	5
9	**2i**	2-FC_6H_4	H	62	15
10	**2j**	2-ClC_6H_4	H	69	8
11	**2k**	2-BrC_6H_4	H	65	12
12	**2l**	2-MeC_6H_4	H	66	11
13	**2m**	2-$MeOC_6H_4$	H	76	14
14	**2n**	3-ClC_6H_4	H	48	10
15	**2o**	3-BrC_6H_4	H	63	16
16	**2p**	3-MeC_6H_4	H	40	9
17	**2q**	3-$MeOC_6H_4$	H	54	10
18	**2r**	Ph	H	56	14
19	**2s**	2-Naph	H	54	16
20	**2t**	2,6-$Cl_2C_6H_3$	H	71	6
21	**2u**	2,4,6-$Me_3C_6H_2$	H	72	8
22	**2v**	2,4-$Cl_2C_6H_4$	H	55	11
23	**2w**	Pyridin-2-yl	H	29	ND[c]
24	**2x**	Funan-2-yl	H	trace	10
25	**2y**	1*H*-indol-3-yl	H	-	-
26	**2z**	*n*-Pentyl	H	31	6
27	**2aa**	Ph	Ph	32	42
28	**2ab**	Ph	Me	27	7
29	**2ac**	Bn	Me	trace	ND
30	**2ad**	Ph	OMe	-	-

[a]Reaction conditions: **1a** (0.2 mmol) and **2** (0.8 mmol) in 3 mL of anhydrous solvent in a capped microwave reaction tube filled with N_2 were heated under microwave irradiation. [b]Yield of the isolated product. [c]ND = not determined.

With the optimal conditions in hand, the scope and generality of aldehydes and ketones were investigated and the results are summarized in Table 2. First of all, the reactions of different *para*-substituted benzaldehydes **2b**-**2h** were conducted; both weak electron-withdrawing and electron-donating *para*-substituted benzaldehydes gave the corresponding products

3a-3h in moderate to good yields. Most electron-donating and weak electron-withdrawing *para*-substituted benzaldehydes gave the desired products in higher yields than those with strong electron-withdrawing *para*-substituents (Table 2, entries 1–8). All *ortho*-substituted benzaldehydes **2i-2m** worked well, producing the desired products **3i-2m** in good yields varied from 62–76% (Table 2, entries 9–13). *Meta*-substituted benzaldehydes **2n-2q** were suitable substrates, resulting in the products **3n-2q** in satisfactory yields of 40–63% (Table 2, entries 14–17). Benzaldehyde **2r** and naphthalene-2-carbaldehyde (**2s**) gave rise to the corresponding products **3r** and **3s** in 56% and 54% yields, respectively (Table 2, entries 18 and 19). Polysubstituted benzaldehydes **2t-2v** produced the desired products **3t-3v** in good yields (Table 2, entries 20–22). Furthermore, we also explored several heteroaryl substituted aldehydes **2w-2y**. Only six-membered heteroatom aromatic pyridine-2-carbaldehyde (**2w**) generated the desired product **3w** in 29% yield (Table 2, entry 23). Neither funan-2-carbaldehyde (**2x**) nor 1*H*-indole-3-carbaldehyde (**2y**) worked (Table 2, entries 24 and 25). Aliphatic aldehyde hexanal (**2z**) was tested, affording the desired product **3z** in 31% yield (Table 2, entry 26).

Table 3. Scopes of Diazo Compounds **1**

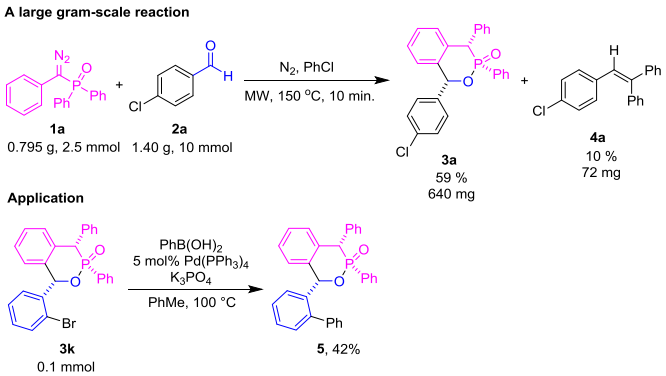


[a]Reaction conditions: **1** (0.2 mmol) and **2a** (0.8 mmol) in 3 mL of anhydrous solvent in a capped microwave reaction tube filled with N_2 were heated under microwave irradiation. [b]Yield of the isolated product. [c]The ratio of products **3** was determined on the basis of the ^{31}P-NMR analysis and the structures of the isomeric products were assigned on the basis of the reaction mechanism.

Besides aldehydes, ketones **2aa-2ac** and ester **2ad** were examined in the reaction as well (Table 2, entries 27–30). Benzophenone (**2aa**) and acetophenone (**2ab**) gave rise to the corresponding products **3aa** and **3ab** in 32% and 27% yields, respectively (Table 2, entries 27 and 28). However, neither 1-phenylacetone nor methyl benzoate worked (Table 2, entries 29 and 30).

The scope of the phosphene precursors, (diazo(aryl)methyl)diarylphosphine oxides **1** were evaluated (Table 3). The reaction of (diazo(2-fluorophenyl)methyl)diphenylphosphine oxide (**1b**) and 4-chlorobenzaldehyde (**2a**) generated the desired products in 59% yield in a pair of isomers **3ad** and **3ad'** in a ratio of 99:1, showing an excellent regioselectivity because 2-fluorophenyl group could not locate in the same plane with the C=C double bond of the phosphine due to steric hindrance (*vide post*). The reaction of (diazo(4-methylphenyl)methyl)diphenylphosphine oxide (**1c**) and aldehyde **2a** produced a pair of isomeric benzo-δ-phospholactone derivatives **3ae** and **3ae'** in 28% yield and 57:43 ratio. The reaction of (diazo(phenyl)methyl)di(4-methylphenyl)phosphine oxide (**1d**) and aldehyde **2a** only generated a trace amount of benzo-δ-phospholactones **3af** and **3af'** possibly because more electron-rich di(4-methylphenyl)phenylphosphene difficultly underwent the nucleophilic addition with aldehyde **2a** (*vide post*). However, the relatively electron-deficient di(4-chlorophenyl)phenylphosphene generated from diazo(phenyl)methyl)di(4-chlorophenyl)phosphine oxide (**1e**) produced a pair of benzo-δ-phospholactones **3ag** and **3ag'** in a moderate yield of 53% in a ratio of 71:29.

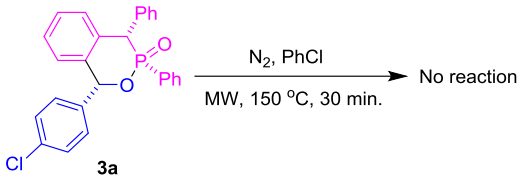
A large gram-scale preparation of product **3a** was carried out, affording in 59% yield, and a further application of product **3k** was conducted in the Suzuki coupling with phenylboronic acid, affording the desired product **5** in 42% yield (Scheme 2).



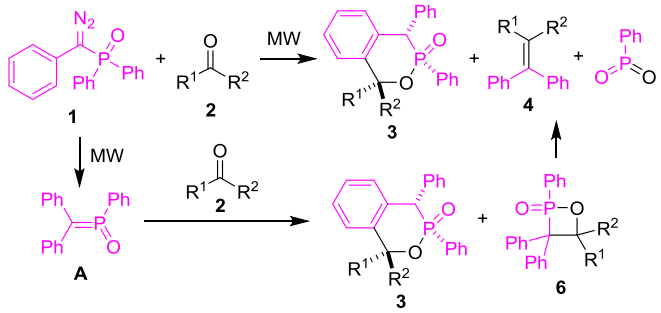
Scheme 2. Gram scaled reaction and application

In each of the reactions, the corresponding substituted 1,1-diarylalk-1-ene derivatives were obtained in low yields ranged from 6–18% as byproducts. To verify the generation pathway of

1,1-diarylalk-1-enes. Pure product **3a** was treated under the reaction conditions (Scheme 3). No reaction was observed, indicating that 1,1-diarylalk-1-enes did not generated from the corresponding products **3** under the reaction conditions (Scheme 4).



Scheme 3. Control Experiment.

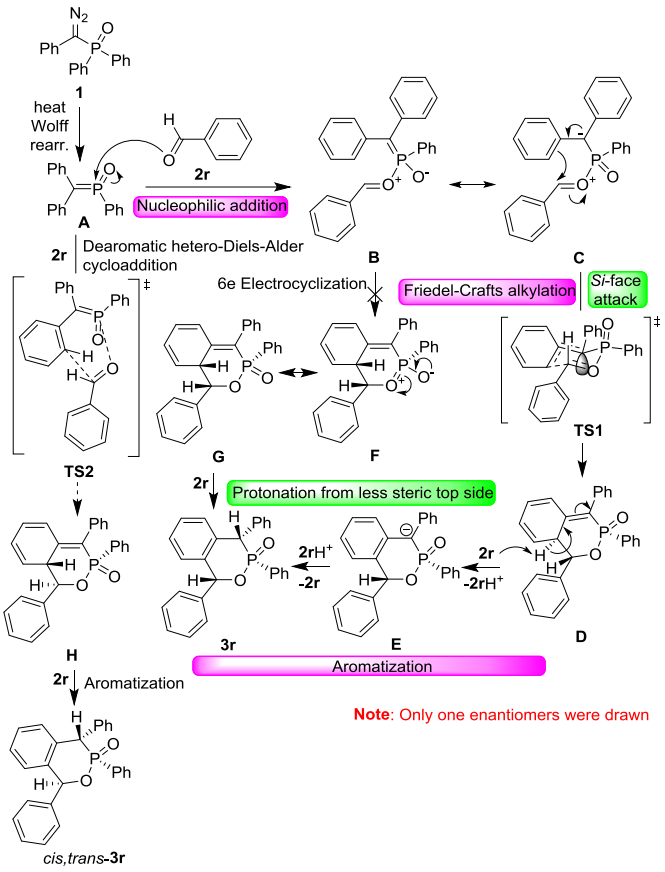


Scheme 4. Periselective annulation of phosphenes with aldehydes and ketones.

Kawashima and co-workers prepared 1,2-oxaphosphetane 2-oxides through esterification of β-hydroxyalkylphosphinic acids and investigated their thermal stability. They found that 1,2-oxaphosphetane 2-oxides were thermal instable and fragmented into the corresponding alkenes and phosphonic acid derivatives after treatment with ethanol.[10,11] On the basis of the control experiment and the results mentioned above, we concluded that the reaction of (diazo)phenylmethyl(diphenyl)phosphine oxide (**1a**) first underwent a Wolff rearrangement to generate diphenyl(phenyl)phosphene (**A**), which further reacted with aldehydes and ketones to give (4+2) annulation products, benzo-δ-phospholactones **3**, periselectively companying with (2+2) annulation product β-phospholactones, 1,2-oxaphosphetane 2-oxides **6**, as minor products. However, 1,2-oxaphosphetane 2-oxides **6** were instable and fragmented into the corresponding alkenes **4** and phenylphosphine dioxide,[10,11] which was converted into phenylphosphonic acid during workup (Scheme 4).

The reaction mechanism is proposed on the basis of the previous results on the reaction of phosphenes with cyclic imines[12] and the stereostructure of products **3** (Scheme 5). Diazo(phenyl)methyl(diphenyl)phosphine oxide (**1a**) first undergoes a Wolff rearrangement under microwave heating to generate diphenylmethylidene(phenyl)phosphine oxide (phosphene **A**). The oxygen atom of benzaldehyde (**2r**) nucleophilically attacks the phosphene **A** to generate zwitterionic intermediate **B**, which resonates into another zwitterionic intermediate **C**. The electron-rich phenyl group in the benzylcarbanion in **C** nucleophilically attacks the carbonyl carbon (intramolecular Friedel-Craft alkylation) from the *Si*-face of the benzaldehyde (**2r**) through a chair-like six-membered ring transition state **TS1**, in which three phenyl groups locate on the equatorial bond, to generate cyclized intermediate **D**. Intermediate **D** further aromatizes into the final product **3r** in the presence of benzaldehyde (**2r**), which services as a base here. In the last protonation step, the acid protonated benzaldehyde (**2r**H$^+$) accesses the carbanion from less steric top side, yielding product **3r** with the indicated stereostructure (Scheme 5). The strong electron-withdrawing *para*-substituted benzaldehydes give rise to the corresponding products in lower yields than those with electron-donating substituents, indicating that the carbonyl group nucleophilic attack step should be the rate-limiting step.

For the phosphenes with two different aryl groups, the electron-rich ones favor nucleophilically attacks the carbonyl carbon (intramolecular Friedel-Craft alkylation), resulting in the formation of major regiomers of products **3**.



Scheme 5. Plausible mechanism for the formation of 1,3,4-triphenyl-1,4-dihydrobenzo[*d*][1,2]oxaphosphinine 3-oxide (**3r**).

There are other two possible pathways to generate product **3r**. One is that the intermediate **B** undergoes a disrotatary 6e electrocyclization to yield intermediate **F**, which can aromatize into product **3r** through intermediate **G**. Dearomatic hetero-Diels-Alder cycloaddition of the phosphene **A** and benzaldehyde (**2r**) is another possible pathway through transition state **TS2**. However, the cycloaddition would give intermediate **H**, which would aromatize into *cis,trans*-**3r** rather than product **3r** (Scheme 5). Arylmethylphosphonochloridate-generated arylphosphenes also underwent a stepwise annulation with α,β-

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unsaturated ketones rather than cycloaddition.[5] Thus, the process of stepwise nucleophilic additions and aromatization is more reasonable mechanism.

Conclusions

We developed a microwave-assisted reaction of (diazo(aryl)methyl)(diaryl)phosphine oxides with aldehydes and ketones for the improved preparation of benzo-δ-phospholactones from phosphene chemistry. Under microwave irradiation, (diazo(aryl)methyl)(diaryl)phosphine oxides first undergoes a Wolff rearrangement to form diaryl (aryl)phosphenes, which further react with aldehydes and ketones to afford benzo-δ-phospholactones and β-phospholactones. The latter are instable and fragment into 1,1-diarylalk-1-enes and phenylphosphine dioxide under reaction conditions. The periselectivity in the annulation shows that the reaction of diaryl(aryl)phosphenes with aldehydes and ketones favors the phosphene phenyl participating (4+2) annulation with aldehydes and ketones over (2+2) annulation of the C=P bond of the phosphenes with them. Carbocyclic aromatic aldehydes show more activity than heteroaryl aldehydes, aliphatic aldehydes, and ketones.

Experimental

General Information

Melting points were measured on a melting point apparatus and are uncorrected. ^{1}H, ^{13}C, ^{31}P, and ^{19}F NMR spectra were recorded on a 400 MHz NMR spectrometer. Chemical shifts are reported in ppm and referenced to tetramethylsilane (TMS) as internal standards (for $CDCl_3$, tetramethylsilane 0 ppm for ^{1}H and $CDCl_3$ 77.00 ppm for ^{13}C). IR spectra (KBr pellets, ν (cm^{-1})) were taken on an FT-IR spectrometer. The high-resolution mass spectra were obtained under ESI ionization using an LC/MSD TOF mass spectrometer. Microwave reactions were performed with a CEM Discover microwave reactor. Column chromatography was carried out on silica gel (200–300 mesh) with a mixture of petroleum ether (PE, 60 °C–90 °C) and ethyl acetate (EA) as the eluent. All reactions were followed by thin-layer chromatography (TLC) where practical, using silica gel 60 F254 fluorescent treated silica gel plates, which were visualized under UV light (254 nm). Commercial-grade reagents and solvents were used without further purification unless otherwise noted, anhydrous solvent was purified with the standard process. Liquid aldehydes were washed with saturated $NaHCO_3$ for several times and dried over anhydrous Na_2SO_4 before using. (diazo)arylmethyl(diaryl)phosphine oxide **1** used in this work were synthesized according the method from reported procedures.[3e,12,13]

Procedure for the Synthesis of (Diazo)phenylmethyl(diphenyl)phosphine oxide (1a).

Benzaldazine[13] (5 mmol, 0.75 g) and diphenylphosphine oxide (10 mmol, 2.02 g) were dissolved in 40 mL of toluene. The solution was stirred at room temperature overnight and a large amount of white solid was formed during the time. The resulting solid was filtered off and washed with petroleum ether for several times. The obtained solid was dissolved in 40 mL of tetrahydrofuran. After addition of *p*-toluene sulfonic acid hydrate (12 mmol, 2.28 g), the mixture was stirred at room temperature for 5 h. The resulting solid was filtered off and washed with tetrahydrofuran for several times. The obtained solid was dissolved in 30 mL of 15% aqueous ammonia, and the mixture was stirred at room temperature for 1 h. The mixture was extracted with chloroform (3 × 20 mL). The combined organic phase was dried over anhydrous sodium sulfate. After removal of part of the solvent, isoamyl nitrite (12 mmol, 1.44 g) and glacial acetic acid (5 mmol, 0.3 mL) were added. After refluxing for 1 h, the mixture was washed successively with saturated $NaHCO_3$ solution and brine, dried over anhydrous sodium sulfate, and concentrated. The residue was purified by column chromatography on silica gel with petroleum and ethyl acetate (PE:EA = 5:1 to 3:1, *v/v*) as eluent.

(Diazo(phenyl)methyl)diphenylphosphine oxide (1a)

Orange crystals (1.02 g, 32%); mp. 162–164 °C (Lit.[3e] mp. 155–156 °C). IR (KBr) ν (cm^{-1}) 3055, 2923, 2073, 1594, 1493, 1438, 1196, 1117, 1099, 951. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (m, 4H), 7.60 – 7.54 (m, 2H), 7.53 – 7.46 (m, 4H), 7.29 – 7.21 (m, 4H), 7.11 – 7.06 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.6 (d, J = 2.4 Hz), 131.8 (d, J = 10.2 Hz), 130.8 (d, J = 113.2 Hz), 129.2, 128.9 (d, J = 12.9 Hz), 127.2 (d, J = 7.6 Hz), 125.3, 123.8 (d, J = 3.5 Hz), 52.8 (d, J = 119.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.64. HRMS (ESI) calcd for $C_{19}H_{16}N_2OP^+$ $[M+H]^+$ *m/z*: 319.0995; found 319.0990.

General Procedure for the Synthesis of δ-Phospholactones 3

Diazo compound **1** (0.2 mmol) and aldehydes **2** (0.8 mmol) were added into an 8 mL microwave tube. The tube was charged with N_2 and added 3 mL of dry PhCl. The resultant mixture was stirred in a microwave reactor for 10 min at 150 °C. After cooling to room temperature, PhCl was removed and the residue was subjected to flash column chromatography (PE:CH_2Cl_2 = 5:1, *v/v* to PE:EA = 5:1, *v/v* to PE:EA = 1:1, *v/v*) to afford alkenes **4** and phospholactones **3**.

***rel*-(1*R*,3*R*,4*S*)-1-(4-Chlorophenyl)-3,4-diphenyl-1,4-dihydrobenzo[*d*][1,2]oxaphosphinine 3-oxide (3a)**

Colorless crystals (56 mg, 66%). mp. 263–265 °C (Lit.[3e] mp. 243–245 °C). IR (KBr) ν (cm^{-1}) 3059, 2845, 1599, 1233, 1121, 1090, 980, 804. ^{1}H NMR(400 MHz, $CDCl_3$) δ 7.52 – 7.41 (m, 5H), 7.37 – 7.28 (m, 2H), 7.27 – 7.18 (m, 4H), 7.18 – 7.07 (m, 4H), 6.88 – 6.82 (m, 2H), 6.78 (d, J = 7.4 Hz, 1H), 6.74 (d, J = 5.9 Hz, 1H), 4.80 (d, J = 24.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.2 (d, J = 6.3 Hz), 137.0 (d, J = 9.3 Hz), 134.8, 134.5 (d, J = 4.5 Hz), 134.2 (d, J = 5.1 Hz), 132.7, 132.6, 130.3 (d, J = 5.3 Hz), 129.8 (d, J = 9.2 Hz), 129.7, 129.0, 128.7, 128.4, 128.3 (d, J = 140.6 Hz), 128.0 (d, J = 13.3 Hz), 127.3 (d, J = 2.5 Hz), 127.1, 126.8, 78.0 (d, J = 6.0 Hz), 49.4 (d, J = 81.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 35.58. HRMS (ESI) calculated for $C_{26}H_{21}ClO_2P^+$ $[M+H]^+$ 431.0962, found 431.0964.

rel-(1*R*,3*R*,4*S*)-1-(4-Bromophenyl)-3,4-diphenyl-1,4-dihydrobenzo[d][1,2]oxaphosphinine 3-oxide (3b)

Colorless crystals (58 mg, 61%). mp. 238–239 °C. IR (KBr) *v* (cm^{-1}) 3060, 2844, 1490, 1455, 1438, 1233, 1122, 978, 890. ^{1}H NMR(400 MHz, $CDCl_3$) *δ* 7.63 (d, *J* = 7.7 Hz, 2H), 7.49 – 7.39 (m, 3H), 7.37 – 7.29 (m, 2H), 7.28 – 7.08 (m, 8H), 6.85 (d, *J* = 6.8 Hz, 2H), 6.78 (d, *J* = 7.4 Hz, 1H), 6.72 (d, *J* = 5.7 Hz, 1H), 4.80 (d, *J* = 24.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 137.6 (d, *J* = 9.1 Hz), 137.1 (d, *J* = 6.2 Hz), 134.6 (d, *J* = 4.6 Hz), 134.2 (d, *J* = 5.0 Hz), 132.7, 132.6, 132.0, 130.3 (d, *J* = 5.3 Hz), 130.0, 129.9 (d, *J* = 9.2 Hz), 128.7, 128.4 (d, *J* = 1.6 Hz), 128.2 (d, *J* = 140.1 Hz), 128.0 (d, *J* = 13.3 Hz), 127.3 (d, *J* = 2.5 Hz), 127.1, 126.8, 123.0, 78.0 (d, *J* = 5.9 Hz), 49.5 (d, *J* = 81.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) *δ* 35.58. HRMS (ESI) calcd for $C_{26}H_{21}BrO_2P^+$ $[M+H]^+$ *m/z*: 475.0457; found 475.0461.

rel-(1*R*,3*R*,4*S*)-1-(4-Fluorophenyl)-3,4-diphenyl-1,4-dihydrobenzo[*d*][1,2]oxaphosphinine 3-oxide (3c)

Colorless crystals (46 mg, 55%). mp. 218–219 °C. IR (KBr) *v* (cm^{-1}) 3062, 2848, 1511, 1231, 1157, 1121, 978, 888. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.58 – 7.50 (m, 2H), 7.48 – 7.40 (m, 1H), 7.37 – 7.29 (m, 2H), 7.28 – 7.08 (m, 10H), 6.86 (d, *J* = 6.7 Hz, 2H), 6.79 (d, *J* = 7.5 Hz, 1H), 6.75 (d, *J* = 5.8 Hz, 1H), 4.80 (d, *J* = 24.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 162.9 (d, $J_{C\text{-}F}$ = 248.1 Hz), 137.4 (d, *J* = 6.3 Hz), 134.7 (d, *J* = 4.5 Hz), 134.5 (d, *J* = 3.1 Hz), 134.4 (d, *J* = 3.2 Hz), 134.2 (d, *J* = 5.2 Hz), 132.7, 132.6, 132.6 (d, *J* = 2.7 Hz), 130.3 (d, *J* = 5.3 Hz), 130.2 (d, *J* = 8.3 Hz), 129.9 (d, *J* = 9.1 Hz), 128.7, 128.4 (d, *J* = 1.7 Hz), 128.3 (d, $J_{C\text{-}P}$ = 140.1 Hz), 128.0 (d, *J* = 13.3 Hz), 127.3 (d, *J* = 2.7 Hz), 127.1, 126.9, 115.8 (d, *J* = 21.7 Hz), 78.0 (d, *J* = 6.0 Hz), 49.4 (d, *J* = 81.2 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) *δ* -112.50. ^{31}P NMR (162 MHz, $CDCl_3$) *δ* 35.60. HRMS (ESI) calculated for $C_{26}H_{21}FO_2P^+$ $[M+H]^+$ 415.1258, found 415.1264.

rel-(1*R*,3*R*,4*S*)-1-(4-Methylphenyl)-3,4-diphenyl-1,4-dihydrobenzo[*d*][1,2]oxaphosphinine 3-oxide (3d)

Colorless crystals (52 mg, 63%). mp. 272–273 °C (Lit.[3e] mp. 241–242 °C). IR (KBr) *v* (cm^{-1}) 3060, 2920, 1439, 1232, 1121, 976. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.47 – 7.40 (m, 3H), 7.38 – 7.27 (m, 4H), 7.26 – 7.06 (m, 8H), 6.91 – 6.80 (m, 3H), 6.72 (d, *J* = 5.6 Hz, 1H), 4.79 (d, *J* = 24.2 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 138.8, 137.7 (d, *J* = 6.2 Hz), 135.7 (d, *J* = 9.2 Hz), 135.0 (d, *J* = 4.6 Hz), 134.1 (d, *J* = 5.2 Hz), 132.7 (d, *J* = 9.2 Hz), 132.5 (d, *J* = 2.0 Hz), 130.3 (d, *J* = 5.3 Hz), 129.8 (d, *J* = 9.2 Hz), 129.4, 128.44 (d, *J* = 140.1 Hz), 128.4, 128.3, 127.9 (d, *J* = 13.3 Hz), 127.1, 127.0, 78.7 (d, *J* = 6.2 Hz), 49.4 (d, *J* = 81.3 Hz), 21.3. ^{31}P NMR (162 MHz, $CDCl_3$) *δ* 35.48. HRMS (ESI) calculated for $C_{27}H_{24}O_2P^+$ $[M+H]^+$ 411.1508, found 411.1502.

rel-(1*R*,3*R*,4*S*)-1-(4-Isopropylphenyl)-3,4-diphenyl-1,4-dihydrobenzo[*d*][1,2]oxaphosphinine 3-oxide (3e)

Colorless crystals (57 mg, 65%). mp. 123–125 °C. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.51 – 7.44 (m, 2H), 7.44 – 7.32 (m, 5H), 7.29 – 7.05 (m, 8H), 6.90 – 6.84 (m, 3H), 6.74 (d, *J* = 5.6 Hz, 1H), 4.79 (d, *J* = 23.9 Hz, 1H), 2.97 (h, *J* = 6.9 Hz, 1H), 1.31 (s, 3H), 1.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 149.6, 137.7 (d, *J* = 6.3 Hz), 136.0 (d, *J* = 9.0 Hz), 135.2 (d, *J* = 5.0 Hz), 134.1 (d, *J* = 5.2 Hz), 132.7 (d, *J* = 9.3 Hz), 132.4 (d, *J* = 2.4 Hz), 130.3 (d, *J* = 5.3 Hz), 129.9 (d, *J* = 9.1 Hz), 128.42 (d, *J* = 139.9 Hz), 128.36, 128.3 (d, *J* = 1.8 Hz), 127.9 (d, *J* = 13.2 Hz), 127.2, 127.1 (d, *J* = 2.6 Hz), 127.0, 126.8, 78.7 (d, *J* = 6.2 Hz), 49.4 (d, *J* = 81.4 Hz), 33.9, 23.9. ^{31}P NMR (162 MHz, $CDCl_3$) *δ* 35.50. HRMS (ESI) calcd for $C_{29}H_{28}O_2P^+$ $[M+H]^+$ *m/z*: 439.1821; found 439.1826.

rel-(1*R*,3*R*,4*S*)-1-(4-Methoxyphenyl)-3,4-diphenyl-1,4-dihydrobenzo[d][1,2]oxaphosphinine 3-oxide (3f)

Colorless crystals (40 mg, 47%). mp. 243–244 °C (Lit.[3e] mp. 271 °C). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.50 – 7.45 (m, 2H), 7.44 – 7.40 (m, 1H), 7.37 – 7.32 (m, 2H), 7.26 – 7.09 (m, 8H), 7.04 – 7.00 (m, 2H), 6.91 – 6.82 (m, 3H), 6.71 (d, *J* = 5.5 Hz, 1H), 4.77 (d, *J* = 24.0 Hz, 1H), 3.87 (s, 3H). ^{31}P NMR (162 MHz, $CDCl_3$) *δ* 35.43. HRMS (ESI) calculated for $C_{27}H_{24}O_3P^+$ $[M+H]^+$ 427.1458, found 427.1454.

rel-(1*R*,3*R*,4*S*)-4-(3-Oxido-3,4-diphenyl-1,4-dihydrobenzo[*d*][1,2]oxaphosphinin-1-yl)benzonitrile (3g)

Colorless crystals (40 mg, 48%). mp. 274–275 °C. IR (KBr) *v* (cm^{-1}) 3061, 2925, 2851, 2229, 1599, 1439, 1233, 1121, 986, 863. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.81 (d, *J* = 7.6 Hz, 2H), 7.69 (d, *J* = 7.6 Hz, 2H), 7.53 – 7.42 (m, 1H), 7.36 – 7.21 (m, 6H), 7.20 – 7.10 (m, 4H), 6.89 – 6.78 (m, 3H), 6.71 (d, *J* = 7.6 Hz, 1H), 4.84 (d, *J* = 24.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 143.4 (d, *J* = 9.2 Hz), 136.5 (d, *J* = 6.2 Hz), 134.3 (d, *J* = 5.1 Hz), 134.1 (d, *J* = 4.6 Hz), 132.8 (d, *J* = 2.3 Hz), 132.7, 132.6, 130.3 (d, *J* = 5.3 Hz), 129.9 (d, *J* = 8.9 Hz), 129.0, 128.9, 128.5 (d, *J* = 1.8 Hz), 128.1 (d, *J* = 13.3 Hz), 128.0 (d, *J* = 141.2 Hz), 127.4 (d, *J* = 2.6 Hz), 127.3, 126.4, 118.4, 112.9, 77.6 (d, *J* = 5.9 Hz), 49.5 (d, *J* = 80.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) *δ* 35.81. HRMS (ESI) calculated for $C_{27}H_{21}NO_2P^+$ $[M+H]^+$ 422.1304, found 422.1312.

rel-(1*R*,3*R*,4*S*)-1-(4-Nitrophenyl)-3,4-diphenyl-1,4-dihydrobenzo[*d*][1,2]oxaphosphinine 3-oxide (3h)

Yellow crystals (41 mg, 46%). mp. 277–278 °C. IR (KBr) *v* (cm^{-1}) 3361, 2975, 2894, 1523, 1349, 1266, 1232, 1089, 1049, 880, 858. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.37 (d, *J* = 7.8 Hz, 2H), 7.77 (t, *J* = 13.8 Hz, 2H), 7.54 – 7.43 (m, 1H), 7.37 – 7.11 (m, 10H), 6.86 (t, *J* = 8.0 Hz, 3H), 6.71 (d, *J* = 7.6 Hz, 1H), 4.86 (d, *J* = 25.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 148.2, 145.2 (d, *J* = 9.2 Hz), 136.4 (d, *J* = 6.2 Hz), 134.3 (d, *J* = 5.2 Hz), 134.0 (d, *J* = 4.4 Hz), 132.9 (d, *J* = 2.1 Hz), 132.7 (d, *J* = 9.3 Hz), 130.4 (d, *J* = 5.3 Hz), 129.9 (d, *J* = 8.9 Hz), 129.12, 129.08, 128.5 (d, *J* = 1.5 Hz), 128.1 (d, *J* = 13.3 Hz), 127.9 (d, *J* = 139.8 Hz), 127.5 (d, *J* = 2.5 Hz), 127.3, 126.4, 124.0, 77.4 (d, *J* = 6.2 Hz), 49.5 (d, *J* = 80.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) *δ* 35.88. HRMS (ESI) calcd for $C_{26}H_{21}NO_4P^+$ $[M+H]^+$ *m/z*: 442.1203; found 442.1208.

rel-(1*S*,3*R*,4*S*)-1-(2-Fluorophenyl)-3,4-diphenyl-1,4-dihydrobenzo[*d*][1,2]oxaphosphinine 3-oxide (3i)

Colorless crystals (51 mg, 62%). mp. 251–252 °C. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.61 (td, *J* = 7.5, 1.5 Hz, 1H), 7.50 – 7.42 (m, 2H), 7.40 – 7.08 (m, 12H), 7.04 (d, *J* = 6.5 Hz, 1H), 6.91 – 6.81 (m, 3H), 4.83 (d, *J* = 25.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 160.5 (d, $J_{C\text{-}F}$ = 249.0 Hz), 136.8 (d, *J* = 5.8 Hz), 134.3 (d, *J* = 5.0 Hz), 134.2 (d, *J* = 4.6 Hz), 132.9 (d, *J* = 9.3 Hz), 132.7 (d, *J* = 2.9 Hz),

130.8 (d, *J* = 8.3 Hz), 130.6 (d, *J* = 5.5 Hz), 129.8 (d, *J* = 3.4 Hz), 129.5 (d, *J* = 8.9 Hz), 128.7, 128.5 (d, *J* = 2.6 Hz), 128.4 (d, $J_{C\text{-}P}$ = 140.5 Hz), 128.1 (d, *J* = 13.2 Hz), 127.4 (d, *J* = 3.2 Hz), 127.3, 126.1, 125.8 (dd, $J_{C\text{-}F,\ C\text{-}P}$ = 12.8, 9.6 Hz), 124.8 (d, *J* = 3.6 Hz), 115.9 (d, *J* = 21.2 Hz), 73.3 (dd, $J_{C\text{-}P,\ C\text{-}F}$ = 5.9, 3.6 Hz), 49.7 (d, *J* = 80.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) *δ* 35.60. ^{19}F NMR (377 MHz, $CDCl_3$) *δ* -116.07. HRMS (ESI) calculated for $C_{26}H_{21}FO_2P^+$ $[M+H]^+$ 415.1258, found 415.1262.

***rel*-(1*S*,3*R*,4*S*)-1-(2-Chlorophenyl)-3,4-diphenyl-1,4-dihydrobenzo[*d*][1,2]oxaphosphinine 3-oxide (3j)**

Colorless crystals (59 mg, 70%). mp. 268–269 °C. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.72 – 7.66 (m, 1H), 7.53 – 7.09 (m, 15H), 6.91 – 6.84 (m, 2H), 6.77 – 6.70 (m, 1H), 4.91 (d, *J* = 27.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 136.8 (d, *J* = 5.3 Hz), 135.9 (d, *J* = 9.8 Hz), 134.7 (d, *J* = 4.8 Hz), 133.3, 133.0 (d, *J* = 9.5 Hz), 132.7 (d, *J* = 1.9 Hz), 130.8 (d, *J* = 5.6 Hz), 129.9, 129.5, 128.7, 128.6 (d, *J* = 140.5 Hz), 128.4 (d, *J* = 2.5 Hz), 128.1 (d, *J* = 13.4 Hz), 127.52, 127.47 (d, *J* = 2.6 Hz), 127.1, 126.2, 75.1 (d, *J* = 5.4 Hz), 50.0 (d, *J* = 79.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) *δ* 34.95. HRMS (ESI) calcd for $C_{26}H_{21}ClO_2P^+$ $[M+H]^+$ *m/z*: 431.0962; found 431.0970.

***rel*-(1*S*,3*R*,4*S*)-1-(2-bromophenyl)-3,4-diphenyl-1,4-dihydrobenzo[*d*][1,2]oxaphosphinine 3-oxide (3k)**

Colorless crystals (62 mg, 65%). mp. 273–274 °C. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.72 – 7.65 (m, 2H), 7.52 – 7.42 (m, 2H), 7.36 – 7.15 (m, 10H), 7.14 – 7.08 (m, 2H), 6.91 – 6.85 (m, 2H), 6.72 (d, *J* = 7.4 Hz, 1H), 4.92 (d, *J* = 27.9 Hz, 1H). ^{31}P NMR (162 MHz, $CDCl_3$) *δ* 34.78. HRMS (ESI) calcd for $C_{26}H_{21}BrO_2P^+$ $[M+H]^+$ *m/z*: 475.0457; found 475.0450.

***rel*-(1*R*,3*R*,4*S*)-1-(2-Methylphenyl)-3,4-diphenyl-1,4-dihydrobenzo[*d*][1,2]oxaphosphinine 3-oxide (3l)**

Colorless crystals (54 mg, 66%). mp. 281–282 °C. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.61 – 7.54 (m, 1H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.37 – 7.10 (m, 13H), 6.96 (d, *J* = 7.2 Hz, 1H), 6.88 (d, *J* = 7.6 Hz, 2H), 6.72 (d, *J* = 7.6 Hz, 1H), 4.89 (d, *J* = 26.7 Hz, 1H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 137.3 (d, *J* = 5.4 Hz), 136.4 (d, *J* = 8.3 Hz), 136.2, 134.9 (d, *J* = 4.9 Hz), 133.8 (d, *J* = 4.5 Hz), 132.9 (d, *J* = 9.1 Hz), 132.6 (d, *J* = 2.8 Hz), 130.7 (d, *J* = 5.6 Hz), 130.5, 128.9 (d, *J* = 8.5 Hz), 128.7 (d, *J* = 141.3 Hz), 128.6 (d, *J* = 4.8 Hz), 128.4 (d, *J* = 2.5 Hz), 128.1, 128.0, 127.3 (d, *J* = 3.1 Hz), 127.0, 126.6, 126.5, 75.5 (d, *J* = 5.0 Hz), 49.9 (d, *J* = 79.8 Hz), 19.5. ^{31}P NMR (162 MHz, $CDCl_3$) *δ* 35.33. HRMS (ESI) calcd for $C_{27}H_{24}O_2P^+$ $[M+H]^+$ *m/z*: 411.1508; found 411.1519.

***rel*-(1*S*,3*R*,4*S*)-1-(2-Methoxyphenyl)-3,4-diphenyl-1,4-dihydrobenzo[*d*][1,2]oxaphosphinine 3-oxide (3m)**

Colorless crystals (65 mg, 76%). mp. 235–236 °C. IR (KBr) *ν* (cm^{-1}) 3062, 2938, 2839, 1602, 1494, 1438, 1249, 1232, 1122, 979, 907. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.58 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.47 – 7.38 (m, 2H), 7.37 – 7.30 (m, 2H), 7.27 – 7.14 (m, 8H), 7.11 – 7.05 (m, 2H), 7.01 (d, *J* = 7.4 Hz, 1H), 6.91 – 6.85 (m, 2H), 6.78 (dd, *J* = 8.3, 6.8 Hz, 1H), 4.85 (d, *J* = 26.9 Hz, 1H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 156.8, 138.0 (d, *J* = 5.3 Hz), 134.5 (d, *J* = 4.7 Hz), 133.8 (d, *J* = 4.4 Hz), 132.9 (d, *J* = 9.2 Hz), 132.4 (d, *J* = 2.0 Hz), 130.7 (d, *J* = 5.4 Hz), 129.8, 128.9 (d, *J* = 140.0 Hz), 128.7, 128.5 (d, *J* = 8.3 Hz), 128.3 (d, *J* = 1.4 Hz), 128.2, 127.9 (d, *J* = 13.3 Hz), 127.2 (d, *J* = 2.3 Hz), 126.9, 126.6 (d, *J* = 9.4 Hz), 126.3, 121.0, 110.7, 73.1 (d, *J* = 5.7 Hz), 55.5, 49.9 (d, *J* = 79.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) *δ* 34.84. HRMS (ESI) calcd for $C_{27}H_{24}O_3P^+$ $[M+H]^+$ *m/z*: 427.1458; found 427.1466.

***rel*-(1*R*,3*R*,4*S*)-1-(3-Chlorophenyl)-3,4-diphenyl-1,4-dihydrobenzo[*d*][1,2]oxaphosphinine 3-oxide (3n)**

Colorless crystals (41 mg, 48%). mp. 209–210 °C. IR (KBr) *ν* (cm^{-1}) 3062, 2848, 1438, 1233, 1121, 983, 866. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.55 (s, 1H), 7.49 – 7.41 (m, 4H), 7.38 – 7.29 (m, 2H), 7.29 – 7.19 (m, 4H), 7.19 – 7.09 (m, 4H), 6.85 (d, *J* = 6.6 Hz, 2H), 6.80 (d, *J* = 7.3 Hz, 1H), 6.73 (d, *J* = 5.9 Hz, 1H), 4.81 (d, *J* = 24.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 140.4 (d, *J* = 9.2 Hz), 137.0 (d, *J* = 6.3 Hz), 134.7, 134.5 (d, *J* = 4.6 Hz), 134.2 (d, *J* = 5.1 Hz), 132.7, 132.6, 130.3 (d, *J* = 5.3 Hz), 130.0, 129.8 (d, *J* = 9.1 Hz), 129.1, 128.7, 128.4 (d, *J* = 1.8 Hz), 128.3, 128.2 (d, *J* = 140.2 Hz), 128.0 (d, *J* = 13.3 Hz), 127.3 (d, *J* = 2.6 Hz), 127.2, 126.8, 126.5, 77.9 (d, *J* = 5.9 Hz), 49.4 (d, *J* = 81.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) *δ* 35.66. HRMS (ESI) calcd for $C_{26}H_{21}ClO_2P^+$ $[M+H]^+$ *m/z*: 431.0962; found 431.0973.

***rel*-(1*R*,3*R*,4*S*)-1-(3-Bromophenyl)-3,4-diphenyl-1,4-dihydrobenzo[*d*][1,2]oxaphosphinine 3-oxide (3o)**

Colorless crystals (60 mg, 63%). mp. 235–236 °C. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.70 (s, 1H), 7.58 (d, *J* = 7.9 Hz, 1H), 7.51 – 7.40 (m, 2H), 7.39 – 7.07 (m, 11H), 6.90 – 6.81 (m, 2H), 6.79 (d, *J* = 7.1 Hz, 1H), 6.73 (d, *J* = 5.9 Hz, 1H), 4.84 (d, *J* = 24.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 140.7 (d, *J* = 9.2 Hz), 137.0 (d, *J* = 6.2 Hz), 134.5 (d, *J* = 4.8 Hz), 134.2 (d, *J* = 5.2 Hz), 132.74, 132.65, 132.1, 131.2, 130.4, 130.3 (d, *J* = 1.9 Hz), 129.8 (d, *J* = 9.0 Hz), 128.8, 128.4 (d, *J* = 2.7 Hz), 128.1 (d, *J* = 140.2 Hz), 128.0 (d, *J* = 13.3 Hz), 127.3 (d, *J* = 3.2 Hz), 127.2 (d, *J* = 0.4 Hz), 127.0, 126.8 (d, *J* = 0.9 Hz), 122.8, 77.9 (d, *J* = 6.2 Hz), 49.4 (d, *J* = 81.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) *δ* 35.65. HRMS (ESI) calcd for $C_{26}H_{21}BrO_2P^+$ $[M+H]^+$ *m/z*: 475.0457; found 475.0467.

***rel*-(1*R*,3*R*,4*S*)-1-(3-Methylphenyl)-3,4-diphenyl-1,4-dihydrobenzo[*d*][1,2]oxaphosphinine 3-oxide (3p)**

Colorless crystals (33 mg, 56%). mp. 192–193 °C. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.44 (td, *J* = 7.5, 1.3 Hz, 1H), 7.40 – 7.31 (m, 5H), 7.28 – 7.07 (m, 9H), 6.91 – 6.85 (m, 2H), 6.83 (d, *J* = 7.2 Hz, 1H), 6.72 (d, *J* = 5.9 Hz, 1H), 4.82 (d, *J* = 24.6 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 138.4, 138.4 (d, *J* = 9.0 Hz), 137.8 (d, *J* = 6.2 Hz), 134.8 (d, *J* = 4.7 Hz), 134.2 (d, *J* = 5.2 Hz), 132.8 (d, *J* = 9.3 Hz), 132.5 (d, *J* = 2.9 Hz), 130.4 (d, *J* = 5.4 Hz), 129.7 (d, *J* = 9.1 Hz), 129.6, 129.0, 128.6, 128.44, 128.41 (d, *J* = 140.3 Hz), 128.3 (d, *J* = 2.6 Hz), 127.9 (d, *J* = 13.4 Hz), 127.2 (d, *J* = 3.1 Hz), 127.1 (d, *J* = 0.9 Hz), 127.0, 125.4, 78.8 (d, *J* = 6.3 Hz), 49.4 (d, *J* = 81.1 Hz), 21.5. ^{31}P NMR (162 MHz, $CDCl_3$) *δ* 35.56. HRMS (ESI) calcd for $C_{27}H_{24}O_2P^+$ $[M+H]^+$ *m/z*: 411.1508; found 411.1497.

***rel*-(1*R*,3*R*,4*S*)-1-(3-Methoxyphenyl)-3,4-diphenyl-1,4-dihydrobenzo[*d*][1,2]oxaphosphinine 3-oxide (3q)**

Colorless crystals (46 mg, 54%). mp. 175–176 °C. IR (KBr) *ν* (cm^{-1}) 3061, 2837, 1599, 1493, 1438, 1231, 1121, 986, 927, 927, 877. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.47 – 7.30 (m, 4H), 7.27 – 7.07

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(m, 10H), 7.01 – 6.97 (m, 1H), 6.89 – 6.83 (m, 3H), 6.72 (d, *J* = 5.7 Hz, 1H), 4.79 (d, *J* = 24.3 Hz, 1H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 159.8, 140.0 (d, *J* = 9.1 Hz), 137.5 (d, *J* = 6.3 Hz), 134.9 (d, *J* = 4.6 Hz), 134.0 (d, *J* = 5.1 Hz), 132.7 (d, *J* = 9.2 Hz), 132.5 (d, *J* = 2.1 Hz), 130.3 (d, *J* = 5.3 Hz), 129.8, 129.7, 128.5, 128.4 (d, *J* = 140.2 Hz), 128.3 (d, *J* = 1.7 Hz), 127.9 (d, *J* = 13.2 Hz), 127.2 (d, *J* = 2.7 Hz), 127.0 (d, *J* = 4.8 Hz), 120.6, 114.1 (d, *J* = 3.4 Hz), 78.6 (d, *J* = 6.1 Hz), 55.3, 49.4 (d, *J* = 81.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) *δ* 35.43. HRMS (ESI) calcd for $C_{27}H_{24}O_3P^+$ $[M+H]^+$ *m/z*: 427.1458; found 427.1448.

***rel*-(1*R*,3*R*,4*S*)-1,3,4-Triphenyl-1,4-dihydrobenzo[*d*][1,2]oxaphosphinine 3-oxide (3r)** [6]

Colorless crystals (45 mg, 56%). mp. 265–266 °C (Sub.) (Lit.[6] mp. 254–257 °C). IR (KBr) *ν* (cm^{-1}) 3060, 2844, 1231, 1121, 976, 887, 848. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.56 (d, *J* = 7.5 Hz, 2H), 7.52 – 7.39 (m, 4H), 7.39 – 7.30 (m, 2H), 7.28 – 7.06 (m, 8H), 6.87 (d, *J* = 6.6 Hz, 2H), 6.81 (d, *J* = 7.5 Hz, 1H), 6.76 (d, *J* = 5.7 Hz, 1H), 4.81 (d, *J* = 24.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 138.5 (d, *J* = 9.0 Hz), 137.6 (d, *J* = 6.3 Hz), 134.8 (d, *J* = 4.5 Hz), 134.2 (d, *J* = 5.0 Hz), 132.7 (d, *J* = 9.2 Hz), 132.5 (d, *J* = 2.1 Hz), 130.4 (d, *J* = 5.3 Hz), 129.7 (d, *J* = 9.1 Hz), 128.9, 128.7, 128.5, 128.4 (d, *J* = 140.2 Hz), 128.3, 128.0, 127.9, 127.2 (d, *J* = 2.5 Hz), 127.0, 78.7 (d, *J* = 6.1 Hz), 49.5 (d, *J* = 81.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) *δ* 35.50.

***rel*-(1*R*,3*R*,4*S*)-1-(Naphthalen-2-yl)-3,4-diphenyl-1,4-dihydrobenzo[*d*][1,2]oxaphosphinine 3-oxide (3s)**

Colorless crystals (48 mg, 54%). mp. 214–215 °C (Lit.[3e] mp. 248-249 °C). IR (KBr) *ν* (cm^{-1}) 3060, 2848, 1599, 1439, 1232, 1121, 986, 950, 905, 813. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.02 (s, 1H), 7.96 (d, *J* = 8.4 Hz, 1H), 7.93 – 7.86 (m, 2H), 7.64 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.57 – 7.51 (m, 2H), 7.46 – 7.36 (m, 3H), 7.28 – 7.21 (m, 3H), 7.19 – 7.10 (m, 5H), 6.96 – 6.88 (m, 3H), 6.81 (d, *J* = 8.0 Hz, 1H), 4.86 (d, *J* = 24.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 137.5 (d, *J* = 6.2 Hz), 135.7 (d, *J* = 9.2 Hz), 134.7 (d, *J* = 4.7 Hz), 134.2 (d, *J* = 5.2 Hz), 133.4, 133.0, 132.7 (d, *J* = 9.2 Hz), 132.5 (d, *J* = 2.8 Hz), 130.4 (d, *J* = 5.4 Hz), 129.7 (d, *J* = 9.0 Hz), 128.7, 128.5, 128.4 (d, *J* = 140.1 Hz), 128.3 (d, *J* = 2.5 Hz), 128.2, 128.0, 127.9 (d, *J* = 3.0 Hz), 127.8, 127.2 (d, *J* = 3.1 Hz), 127.1 (d, *J* = 8.1 Hz), 126.6 (d, *J* = 13.9 Hz), 125.4, 78.9 (d, *J* = 6.2 Hz), 49.5 (d, *J* = 81.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) *δ* 35.54. HRMS (ESI) calculated for $C_{30}H_{24}O_2P^+$ $[M+H]^+$ 447.1508, found 447.1504.

***rel*-(1*R*,3*R*,4*S*)-1-(2,6-Dichlorophenyl)-3,4-diphenyl-1,4-dihydrobenzo[*d*][1,2]oxaphosphinine 3-oxide (3t)**

Colorless crystals (66 mg, 76%). mp. 264–265 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) *δ* 7.56 (d, *J* = 7.6 Hz, 1H), 7.52 – 7.37 (m, 5H), 7.35 – 7.18 (m, 5H), 7.17 – 7.05 (m, 4H), 6.90 (d, *J* = 7.3 Hz, 2H), 6.81 (d, *J* = 7.5 Hz, 1H), 4.84 (d, *J* = 25.7 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) *δ* 136.7, 136.3, 135.1 (d, *J* = 4.8 Hz), 134.9 (d, *J* = 5.4 Hz), 134.7 (d, *J* = 4.5 Hz), 132.7 (d, *J* = 9.7 Hz), 132.4 (d, *J* = 2.9 Hz), 130.6, 130.5 (d, *J* = 2.6 Hz), 130.2 (d, *J* = 9.6 Hz), 128.5 (d, *J* = 9.3 Hz), 128.2 (d, *J* = 2.8 Hz), 128.0 (d, *J* = 141.5 Hz), 127.8 (d, *J* = 13.5 Hz), 127.2, 127.0 (d, *J* = 3.3 Hz), 125.0, 73.9 (d, *J* = 5.4 Hz), 49.5 (d, *J* = 80.7 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) *δ* 37.89. HRMS (ESI) calcd for $C_{26}H_{20}Cl_2O_2P^+$ $[M+H]^+$ *m/z*: 465.0572; found 465.0581.

***rel*-(1*R*,3*R*,4*S*)-1-Mesityl-3,4-diphenyl-1,4-dihydrobenzo[*d*][1,2]oxaphosphinine 3-oxide (3u)**

Colorless crystals (63 mg, 72%). mp. 264–265 °C. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.44 – 7.35 (m, 3H), 7.27 – 7.06 (m, 9H), 6.95 (s, 2H), 6.91 – 6.86 (m, 2H), 6.83 (d, *J* = 7.6 Hz, 1H), 4.87 (d, *J* = 27.1 Hz, 1H), 2.42 (s, 3H), 2.33 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 138.3 (d, *J* = 11.7 Hz), 137.1, 137.0 (d, *J* = 4.6 Hz), 135.2 (d, *J* = 4.4 Hz), 134.4 (d, *J* = 4.7 Hz), 132.6 (d, *J* = 9.4 Hz), 132.4 (d, *J* = 2.8 Hz), 131.1, 130.7 (d, *J* = 5.5 Hz), 130.2 (d, *J* = 8.4 Hz), 129.2 (d, *J* = 9.0 Hz), 129.1, 128.40 (d, *J* = 140.9 Hz), 128.4, 128.3 (d, *J* = 2.6 Hz), 127.9 (d, *J* = 13.4 Hz), 127.1, 125.5 (d, *J* = 1.1 Hz), 74.4 (d, *J* = 6.3 Hz), 49.8 (d, *J* = 80.0 Hz), 21.9, 20.9, 20.5. ^{31}P NMR (162 MHz, $CDCl_3$) *δ* 37.24. HRMS (ESI) calcd for $C_{29}H_{28}O_2P^+$ $[M+H]^+$ *m/z*: 439.1821; found 439.1816.

***rel*-(1*R*,3*R*,4*S*)-1-(2,4-Dichlorophenyl)-3,4-diphenyl-1,4-dihydrobenzo[*d*][1,2]oxaphosphinine 3-oxide (3v)**

Colorless crystals (51 mg, 55%). mp. 294–295 °C. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.62 (d, *J* = 8.4 Hz, 1H), 7.54 (d, *J* = 2.1 Hz, 1H), 7.52 – 7.45 (m, 1H), 7.42 – 7.38 (m, 1H), 7.33 – 7.08 (m, 11H), 6.91 – 6.82 (m, 2H), 6.71 (d, *J* = 7.1 Hz, 1H), 4.90 (d, *J* = 27.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 136.3 (d, *J* = 5.1 Hz), 135.2, 134.7 (d, *J* = 4.4 Hz), 134.6, 134.0, 132.9 (d, *J* = 9.4 Hz), 132.8 (d, *J* = 3.8 Hz), 130.7 (d, *J* = 5.6 Hz), 130.2, 129.3, 128.9, 128.7 (d, *J* = 8.3 Hz), 128.5 (d, *J* = 2.4 Hz), 128.4 (d, *J* = 140.4 Hz), 128.2, 128.0 (d, *J* = 11.6 Hz), 127.5 (d, *J* = 3.0 Hz), 127.2, 126.0, 74.7 (d, *J* = 5.2 Hz), 49.9 (d, *J* = 79.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) *δ* 35.03. HRMS (ESI) calcd for $C_{26}H_{20}Cl_2O_2P^+$ $[M+H]^+$ *m/z*: 465.0572; found 465.0568.

***rel*-(1*R*,3*R*,4*S*)-3,4-Diphenyl-1-(pyridin-2-yl)-1,4-dihydrobenzo[*d*][1,2]oxaphosphinine 3-oxide (3w)**

Yellow crystals (23 mg, 29%). mp. 244–246 °C. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.78 – 8.73 (m, 1H), 7.84 (td, *J* = 7.7, 1.8 Hz, 1H), 7.65 (d, *J* = 7.9 Hz, 1H), 7.48 – 7.09 (m, 12H), 6.98 – 6.90 (m, 3H), 6.86 (d, *J* = 5.2 Hz, 1H), 4.79 (d, *J* = 23.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 158.1 (d, *J* = 10.3 Hz), 149.3, 137.1, 136.4 (d, *J* = 7.2 Hz), 134.8 (d, *J* = 4.7 Hz), 133.6 (d, *J* = 5.6 Hz), 132.8 (d, *J* = 9.3 Hz), 132.6 (d, *J* = 2.8 Hz), 130.4 (d, *J* = 5.4 Hz), 129.9 (d, *J* = 9.1 Hz), 128.5, 128.29 (d, *J* = 2.7 Hz), 128.25 (d, *J* = 140.2 Hz), 128.0, 127.9, 126.5 (d, *J* = 0.7 Hz), 123.4, 122.4, 79.1 (d, *J* = 6.2 Hz), 49.3 (d, *J* = 81.6 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) *δ* 35.48. HRMS (ESI) calcd for $C_{25}H_{21}NO_2P^+$ $[M+H]^+$ *m/z*: 398.13044; found 398.13040.

***rel*-(1*R*,3*R*,4*S*)-1-Pentyl-3,4-diphenyl-1,4-dihydrobenzo[*d*][1,2]oxaphosphinine 3-oxide (3z)**

Colorless liquid (24 mg, 31%). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.89 –7.82 (m, 2H), 7.67 – 7.59 (m, 2H), 7.58 –7.53 (m, 1H), 7.51 – 7.44 (m, 2H), 7.43 – 7.34 (m, 2H), 7.27 – 7.16 (m, 6H), 6.69 (d, *J* = 4.4 Hz, 1H), 2.31 – 2.12 (m, 2H), 1.40 (dt, *J* = 15.0, 7.5 Hz, 2H), 1.22 – 1.13 (m, 2H), 1.12 – 1.02 (m, 2H), 0.80 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 172.3 (d, *J* = 7.3 Hz), 132.9, 132.5 (d, *J* = 2.1 Hz), 132.4 (d, *J* = 2.1 Hz), 132.3, 132.2, 131.7 (d, *J* = 9.1

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Hz), 131.0, 130.0, 129.3, 128.7 (d, *J* = 4.0 Hz), 128.5 (d, *J* = 4.3 Hz), 128.3 (d, *J* = 4.0 Hz), 72.8 (d, *J* = 85.5 Hz), 34.2, 31.1, 29.8, 24.5, 22.3, 13.9. ^{31}P NMR (162 MHz, $CDCl_3$) δ -50.00. HRMS (ESI) calcd for $C_{25}H_{28}O_2P^+$ $[M+H]^+$ *m/z*: 391.1821; found 391.1822.

rel-(3*R*,4*S*)-1,1,3,4-Tetraphenyl-1,4-dihydrobenzo[*d*][1,2]oxaphosphinine 3-oxide (3aa)

Yellow oil (30 mg, 32%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.49 (m, 1H), 7.44 – 7.29 (m, 13H), 7.27 – 7.22 (m, 4H), 7.19 – 7.13 (m, 1H), 7.09 – 7.05 (m, 3H), 6.85 (dd, *J* = 7.4, 1.6 Hz, 1H), 6.63 – 6.58 (m, 2H), 4.36 (d, *J* = 30.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.1 (d, *J* = 9.5 Hz), 142.5 (d, *J* = 2.0 Hz), 141.4 (d, *J* = 6.3 Hz), 134.9 (d, *J* = 4.5 Hz), 133.2 (d, *J* = 9.2 Hz), 132.6 (d, *J* = 2.8 Hz), 132.0 (d, *J* = 4.8 Hz), 131.3 (d, *J* = 5.9 Hz), 131.2, 129.8, 129.3 (d, *J* = 1.8 Hz), 128.9 (d, *J* = 2.4 Hz), 128.6, 128.5, 128.4, 128.40, 128.39, 128.4, 128.3, 128.2, 127.6 (d, *J* = 2.7 Hz), 126.7 (d, *J* = 1.6 Hz), 91.9 (d, *J* = 8.7 Hz), 50.4 (d, *J* = 77.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.36. HRMS (ESI) calcd for $C_{32}H_{26}O_2P^+$ $[M+H]^+$ *m/z*: 473.1665; found 473.1655.

rel-(1*R*,3*R*,4*S*)-1-Methyl-1,3,4-triphenyl-1,4-dihydrobenzo[*d*][1,2]oxaphosphinine 3-oxide (3ab)

Colorless crystals (22 mg, 27%). mp. 120–122 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.54 (m, 4H), 7.53 – 7.43 (m, 2H), 7.42 – 7.32 (m, 7H), 7.32 – 7.24 (m, 2H), 7.22 – 7.06 (m, 4H), 4.49 (d, *J* = 17.5 Hz, 1H), 3.58 (d, *J* = 10.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.8 (d, *J* = 6.9 Hz), 136.2, 133.1 (d, *J* = 9.4 Hz), 132.1, 132.1, 132.0, 131.2, 129.8 (d, *J* = 126.0 Hz), 129.7, 129.7, 129.6, 129.6, 128.5 (d, *J* = 16.3 Hz), 128.2 (d, *J* = 12.5 Hz), 128.0, 127.8, 127.0 (d, *J* = 15.1 Hz), 54.3 (d, *J* = 94.7 Hz), 51.9 (d, *J* = 6.9 Hz), 29.7. ^{31}P NMR (162 MHz, $CDCl_3$) δ 41.03. HRMS (ESI) calcd for $C_{27}H_{24}O_2P^+$ $[M+H]^+$ *m/z*: 411.1508; found 411.1505.

rel-(1*R*,3*R*,4*S*)-1-(4-Chlorophenyl)-5-fluoro-3,4-diphenyl-1,4-dihydrobenzo[*d*][1,2]oxaphosphinine 3-oxide (3ad')

White solid (53 mg, 59%). mp. 115–117 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.38 (m, 8H), 7.31 – 7.21 (m, 4H), 7.08 (d, *J* = 7.2 Hz, 1H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.89 – 6.72 (m, 4H), 5.17 (d, *J* = 22.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.0 (d, *J* = 5.9 Hz), 159.5 (d, *J* = 5.9 Hz), 137.9 (d, *J* = 8.7 Hz), 136.9 (d, *J* = 6.6 Hz), 135.1, 133.1 (d, *J* = 5.2 Hz), 132.9 (d, *J* = 2.1 Hz), 132.6 (d, *J* = 9.4 Hz), 131.1 (d, *J* = 9.8 Hz), 130.8, 130.1, 129.3, 129.2 (d, *J* = 2.6 Hz), 129.0, 128.5 (dd, $J_{C\text{-}F}$ = 15.0 Hz, $J_{C\text{-}P}$ = 7.4 Hz), 128.07 (d, J = 13.3 Hz), 127.6, 127.2 (d, *J* = 6.7 Hz), 124.2, 124.0 (dd, $J_{C\text{-}F}$ = 14.2 Hz, $J_{C\text{-}P}$ = 4.8 Hz), 115.6 (d, *J* = 22.6 Hz), 78.1 (d, *J* = 5.8 Hz), 41.2 (d, *J* = 83.6 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 35.06. HRMS (ESI) calcd for $C_{26}H_{20}ClFO_2P^+$ $[M+H]^+$ *m/z*: 449.0868; found 449.0872.

rel-(1*R*,3*R*,4*S*)-1-(4-Chlorophenyl)-3-phenyl-4-(4-methylphenyl)-1,4-dihydrobenzo[*d*][1,2]oxaphosphinine 3-oxide (3ae) and (1*R*,3*R*,4*S*)-1-(4-chlorophenyl)-5-methyl-3,4-diphenyl-1,4-dihydrobenzo[*d*][1,2]oxaphosphinine 3-oxide (3ae')

Colorless liquid (24 mg, 28%, **3ae**: **3ae'** = 43:57). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.46 (d, *J* = 8.9 Hz, 7H), 7.44 – 7.28 (m, 9H), 7.24 – 7.10 (m, 8H), 7.07 – 7.05 (m, 2H), 6.99 – 6.94 (m, 3H), 6.84 (d, *J* = 6.8 Hz, 2H), 6.76 (d, *J* = 7.0 Hz, 1H), 6.73 – 6.68 (m, 3H), 6.57 (s, 1H), 4.77 (d, *J* = 10.1 Hz, 1H, **3ae**), 4.71 (d, *J* = 9.4 Hz, 1H, **3ae'**), 2.27 (s, 3H, **3ae**), 2.25 (s, 3H, **3ae'**). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.6 (d, *J* = 6.9 Hz), 137.3, 137.1 (d, *J* = 5.6 Hz), 135.0, 133.1, 133.0, 132.9, 132.8, 131.4 (d, *J* = 3.4 Hz), 131.3, 130.5 (d, *J* = 4.9 Hz), 130.3 (d, *J* = 9.3 Hz), 130.0, 129.9, 129.8 (d, *J* = 5.8 Hz), 129.4 (d, *J* = 12.3 Hz), 129.0 (d, *J* = 13.2 Hz), 128.7 (d, *J* = 9.0 Hz), 128.5 (d, *J* = 4.4 Hz), 128.3 (d, *J* = 4.3 Hz), 128.2 (d, *J* = 4.2 Hz), 128.0, 127.9 (d, *J* = 7.2 Hz), 127.7 (d, *J* = 5.8 Hz), 127.4 (d, *J* = 2.4 Hz), 127.3, 127.0, 126.9, 78.3 (d, *J* = 5.7 Hz), 49.8 (d, *J* = 12.2 Hz), 49.0 (d, *J* = 7.4 Hz), 29.9, 21.4. ^{31}P NMR (162 MHz, $CDCl_3$) δ 35.87, 35.49. HRMS (ESI) calcd for $C_{27}H_{23}ClO_2P^+$ $[M+H]^+$ *m/z*: 445.1119; found 445.1120.

rel-(1*R*,3*R*,4*S*)-1,3,4-Tris(4-chlorophenyl)-1,4-dihydrobenzo[*d*][1,2]oxaphosphinine 3-oxide (3ag) and (1*R*,3*R*,4*S*)-7-chloro-1,3-bis(4-chlorophenyl)-4-phenyl-1,4-dihydrobenzo[*d*][1,2]oxaphosphinine 3-oxide (3ag')

Yellow oil (53 mg, 53%, **3ag**: **3ag'** = 71:29). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.38 (m, 8H), 7.30 – 7.20 (m, 12H), 7.19 – 7.09 (m, 4H), 7.06 (d, *J* = 7.8 Hz, 2H), 6.88 – 6.64 (m, 8H), 4.84 (d, *J* = 25.0 Hz, 1H, **3ag'**), 4.78 (d, *J* = 22.8 Hz, 1H, **3ag**). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.9 (d, *J* = 3.2 Hz), 139.7 (d, *J* = 3.3 Hz), 138.9 (d, *J* = 6.2 Hz), 137.4 (d, *J* = 5.6 Hz), 136.6 (d, *J* = 9.4 Hz), 136.3 (d, *J* = 9.0 Hz), 135.5, 135.2, 134.3, 134.2, 134.1, 133.8 (d, *J* = 4.8 Hz), 133.7 (d, *J* = 3.3 Hz), 133.5, 132.7, 132.6 (d, *J* = 3.8 Hz), 131.9 (d, *J* = 4.7 Hz), 131.6 (d, *J* = 9.4 Hz), 130.3 (d, *J* = 5.1 Hz), 129.8 (d, *J* = 6.8 Hz), 129.5, 129.2, 129.1 (d, *J* = 4.0 Hz), 128.9, 128.7, 128.8 (d, *J* = 10.1 Hz), 128.5, 127.8 (d, *J* = 2.1 Hz), 127.5, 127.4, 127.1, 126.0, 78.6 (d, *J* = 5.8 Hz), 77.8 (d, *J* = 5.9 Hz), 48.8 (d, *J* = 81.4 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 35.06, 34.09. HRMS (ESI) calcd for $C_{26}H_{19}Cl_3O_2P^+$ $[M+H]^+$ *m/z*: 499.0183; found 499.0176.

(2-(4-Chlorophenyl)ethene-1,1-diyl)dibenzene (4a)[14]

Colorless crystals (10 mg, 17%). mp. 79–80 °C ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.40 (m, 8H), 7.35 – 7.29 (m, 2H), 7.20 (d, *J* = 8.6 Hz, 2H), 7.08 (s, 1H), 7.06 (s, 1H), 7.04 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, 143.0, 139.9, 135.8, 132.3, 130.7, 130.2, 128.7, 128.2, 128.1, 127.7, 127.6, 127.5, 126.7.

(2-(4-Bromophenyl)ethene-1,1-diyl)dibenzene (4b)[15]

Yellow crystals (12 mg, 18%). mp. 76–77 °C (Lit.[3e] mp. 77 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 8H), 7.24 (d, *J* = 8.3 Hz, 2H), 7.20 – 7.15 (m, 2H), 6.87 (d, *J* = 7.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.4, 143.0, 139.9, 136.3, 131.1, 131.0, 130.2, 128.8, 128.2, 127.7, 127.6, 127.6, 126.8, 120.5.

(2-(4-Fluorophenyl)ethene-1,1-diyl)dibenzene (4c)[14]

Yellow oil (4 mg, 7%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 8H), 7.22 – 7.15 (m, 2H), 7.01 – 6.95 (m, 2H), 6.92 (s, 1H), 6.86 – 6.77 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, 142.4, 140.1, 133.5, 131.1 (d, *J* = 7.2 Hz), 130.3, 128.7, 128.2, 127.5, 126.9, 115.0, 114.8. ^{19}F NMR (377 MHz, $CDCl_3$) δ -114.83.

(2-(4-Methylphenyl)ethene-1,1-diyl)dibenzene (4d)[16]

Yellow oil (4 mg, 7%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.26 (m, 8H), 7.23 – 7.19 (m, 2H), 6.97 – 6.88 (m, 5H), 2.26 (s, 3H).

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^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 141.7, 140.6, 136.6, 134.5, 130.4, 129.4, 128.7, 128.6, 128.2, 128.1, 127.5, 127.32, 127.29, 21.2.

(2-(4-Methoxyphenyl)ethene-1,1-diyl)dibenzene (4f)[16]

Yellow solid (4 mg, 7%). mp. 83–84 °C (Lit.[3e] mp. 82–83 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 7H), 7.28 – 7.26 (m, 1H), 7.24 – 7.19 (m, 2H), 6.98 – 6.90 (m, 3H), 6.70 – 6.64 (m, 2H), 3.75 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4, 143.6, 140.6, 140.6, 130.8, 130.4, 130.1, 128.7, 128.2, 127.6, 127.4, 127.3, 127.2, 113.4, 55.1.

4-(2,2-Diphenylvinyl)benzonitrile (4g)[15]

Yellow oil (10 mg, 18%). mp. 122–123 °C ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.30 (m, 10H), 7.19 – 7.13 (m, 2H), 7.08 (d, J = 8.0 Hz, 2H), 6.94 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.2, 142.5, 142.1, 139.4, 131.7, 130.1, 129.9, 128.9, 128.3, 128.3, 128.1, 127.8, 126.1, 119.0, 109.7.

(2-(4-Nitrophenyl)ethene-1,1-diyl)dibenzene (4h)[17]

Yellow crystals (3 mg, 5%). mp. 156–157 °C (Lit.[3e] mp. 243–245 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.95 (m, 2H), 7.41 – 7.32 (m, 8H), 7.20 – 7.09 (m, 4H), 7.00 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.0, 145.9, 144.3, 142.4, 139.3, 130.1, 130.0, 128.9, 128.5, 128.4, 128.2, 127.8, 125.7, 123.3.

(2-(2-Fluorophenyl)ethene-1,1-diyl)dibenzene (4i)[18]

Yellow oil (8 mg, 15%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.27 (m, 8H), 7.22 – 7.15 (m, 2H), 7.13 – 7.03 (m, 2H), 7.03 – 6.95 (m, 1H), 6.82 – 6.73 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.0 (d, J = 247.9 Hz), 144.5, 143.1, 140.0, 130.3, 128.5, 128.3 (d, J = 8.6 Hz), 128.2, 127.9, 127.8, 127.5, 125.4 (d, J = 13.2 Hz), 123.2 (d, J = 3.0 Hz), 120.0 (d, J = 4.9 Hz), 115.3, 115.1. ^{19}F NMR (377 MHz, $CDCl_3$) δ -115.68.

(2-(2-Chlorophenyl)ethene-1,1-diyl)dibenzene (4j)[17]

Colorless oil (5 mg, 8%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.31 (m, 6H), 7.25 (t, J = 3.2 Hz, 3H), 7.17 – 7.12 (m, 2H), 7.09 (s, 1H), 7.07 – 7.02 (m, 1H), 6.90 – 6.80 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.6, 142.9, 139.7, 136.2, 134.6, 131.1, 130.6, 129.2, 128.3, 128.2, 128.1, 127.9, 127.5, 125.9, 125.0.

(2-(2-Bromophenyl)ethene-1,1-diyl)dibenzene (4k)[19]

Yellow oil (8 mg, 12%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.52 (m, 1H), 7.39 – 7.31 (m, 5H), 7.27 – 7.22 (m, 3H), 7.16 – 7.09 (m, 2H), 7.02 (s, 1H), 7.00 – 6.89 (m, 2H), 6.85 – 6.79 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.4, 142.8, 139.6, 138.1, 132.4, 131.4, 130.6, 128.24, 128.22, 128.11, 128.05, 127.9, 127.4, 126.5, 125.1.

(2-(2-Methylphenyl)ethene-1,1-diyl)dibenzene (4l)[20]

Yellow oil (6 mg, 11%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.28 (m, 5H), 7.24 – 7.18 (m, 3H), 7.15 – 7.07 (m, 3H), 7.06 – 7.01 (m, 1H), 6.98 (s, 1H), 6.89 – 6.80 (m, 2H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.6, 143.3, 140.2, 137.0, 130.7, 129.7, 129.7, 128.2, 128.1, 127.5, 127.3, 127.1, 126.8, 125.2, 20.2.

(2-(2-Methoxyphenyl)ethene-1,1-diyl)dibenzene (4m)[14]

Yellow oil (8 mg, 14%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.23 (m, 8H), 7.21 – 7.16 (m, 2H), 7.15 – 7.07 (m, 2H), 6.86 – 6.81 (m, 1H), 6.79 – 6.74 (m, 1H), 6.59 (td, J = 7.6, 1.2 Hz, 1H), 3.82 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.8, 143.8, 142.5, 140.6, 130.6, 130.3, 128.3, 128.0, 128.0, 127.3, 127.1, 126.6, 123.3, 119.8, 110.3, 55.4.

(2-(3-Chlorophenyl)ethene-1,1-diyl)dibenzene (4n)[18]

Yellow oil (11 mg, 10%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.29 (m, 8H), 7.22 – 7.15 (m, 2H), 7.10 – 6.98 (m, 3H), 6.91 – 6.84 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.1, 142.9, 139.8, 139.2, 133.8, 130.2, 129.5, 129.1, 128.7, 128.3, 127.8, 127.7, 127.6, 127.5, 126.7, 126.6.

(2-(3-Bromophenyl)ethene-1,1-diyl)dibenzene (4o)[21]

Yellow oil (11 mg, 16%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 8H), 7.24 – 7.15 (m, 4H), 6.97 (t, J = 7.8 Hz, 1H), 6.92 – 6.86 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2, 142.9, 139.7, 139.5, 132.5, 130.2, 129.6, 129.4, 128.7, 128.3, 127.9, 127.8, 127.7, 127.6, 126.4, 122.0.

(2-(3-Methylphenyl)ethene-1,1-diyl)dibenzene (4p)[14]

Colorless oil (5 mg, 9%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.26 (m, 8H), 7.23 – 7.18 (m, 2H), 7.00 (t, J = 7.6 Hz, 1H), 6.96 – 6.90 (m, 2H), 6.85 (d, J = 1.7 Hz, 1H), 6.79 (d, J = 7.7 Hz, 1H), 2.18 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 142.4, 140.5, 137.4, 137.3, 130.5, 130.3, 128.6, 128.3, 128.2, 127.6, 127.4, 127.3, 126.5, 21.3.

(2-(3-Methoxyphenyl)ethene-1,1-diyl)dibenzene (4q)[16]

Yellow oil (6 mg, 10%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 8H), 7.25 – 7.21 (m, 2H), 7.07 (t, J = 7.9 Hz, 1H), 6.96 (s, 1H), 6.72 – 6.63 (m, 2H), 6.55 – 6.48 (m, 1H), 3.50 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 143.2, 142.7, 140.5, 138.6, 130.3, 128.9, 128.7, 128.2, 128.0, 127.5, 127.4, 122.5, 113.7, 113.5, 54.8.

Ethene-1,1,2-triyltribenzene (4r)[14]

Yellow oil (7 mg, 14%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 8H), 7.23 – 7.18 (m, 2H), 7.16 – 7.08 (m, 3H), 7.03 (d, J = 7.3 Hz, 2H), 6.97 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.4, 142.6, 140.3, 137.4, 130.4, 129.5, 128.6, 128.18, 128.15, 127.9, 127.6, 127.5, 127.4, 126.7.

2-(2,2-Diphenylvinyl)naphthalene (4s)[14]

Yellow oil (10 mg, 16%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (dd, J = 6.0, 3.4 Hz, 1H), 7.64 – 7.60 (m, 1H), 7.56 (s, 1H), 7.52 (d, J = 8.6 Hz, 1H), 7.40 – 7.36 (m, 4H), 7.34 – 7.29 (m, 6H), 7.26 – 7.22 (m, 2H), 7.13 (s, 1H), 7.05 (dd, J = 8.6, 1.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.4, 143.0, 140.4, 135.1, 133.3, 132.25, 130.6, 129.1, 128.7, 128.2, 128.0, 127.7, 127.6, 127.5, 127.5, 127.2, 127.1, 125.9, 125.8.

(2-(2,6-Dichlorophenyl)ethene-1,1-diyl)dibenzene (4t)

Yellowish crystals (4 mg, 6%). mp. 78–79 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.33 (m, 5H), 7.21 – 7.13 (m, 5H), 7.09 – 7.01 (m, 3H), 6.74 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.4, 142.2, 139.7, 136.1135.1, 129.7, 128.4, 128.4, 128.2, 128.1, 127.7, 127.6, 127.5, 122.5. HRMS (ESI) calcd for $C_{20}H_{15}Cl_2^+$ $[M+H]^+$ *m/z*: 325.0545; found 325.05450.

(2-Mesitylethene-1,1-diyl)dibenzene (4u)[22]

Yellow oil (5 mg, 8%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.31 (m, 5H), 7.16 – 7.10 (m, 3H), 7.00 – 6.94 (m, 2H), 6.80 (s, 1H), 6.76 (s, 2H), 2.23 (s, 3H), 2.07 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2, 143.6, 140.4, 136.2, 136.0, 133.9, 129.8, 128.4, 128.1, 128.0, 127.7, 127.5, 127.4, 127.1, 21.0, 20.4.

(2-(2,4-Dichlorophenyl)ethene-1,1-diyl)dibenzene (4v)[23]

Yellow oil (7 mg, 11%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 6H), 7.29 – 7.25 (m, 3H), 7.15 – 7.09 (m, 2H), 7.01 (s, 1H), 6.85 (dd, *J* = 8.4, 2.1 Hz, 1H), 6.73 (d, *J* = 8.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.3, 142.6, 139.4, 135.1, 134.8, 132.7, 131.8, 130.5, 129.0, 128.5, 128.3, 128.1, 127.7, 126.3, 123.8.

1,1,2,2-Tetraphenylethene (4aa)[24]

Yellow solid (28 mg, 42%). mp. 244–246 °C (Lit.[24] mp. 222–224 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 – 7.06 (m, 12H), 7.05 – 7.01 (m, 8H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.75, 140.98, 131.35, 127.67, 126.43.

Procedure for the Suzuki Coupling Reaction of Compound 3k

Compound **3k** (0.1 mmol, 47 mg), $PhB(OH)_2$ (0.15 mmol, 19.8 mg), $Pd(PPh_3)_4$ (5 mol%, 7.8 mg), and K_3PO_4 (0.2 mmol, 43 mg) were added into a 8 mL reaction tube. The tube was charged with N_2 and added 1.5 mL of dry PhMe. Then the resultant mixture was stirred in a classic oil bath for 18 h at 100 °C. After cooling to room temperature, the reaction mixture was washed with water, extracted with EA, dried over anhydrous Na_2SO_4. After removal of solvent the residue was subjected to flash column chromatography (PE:EA = 5:1 to 3:1, *v*/*v*) to afford product **5** (20 mg, 42%).

***rel*-(1*R*,3*R*,4*S*)-1-([1,1'-Biphenyl]-2-yl)-3,4-diphenyl-1,4-dihydrobenzo[*d*][1,2]oxaphosphinine 3-oxide (5)**

Yellow crystals (20 mg, 42%). mp. 141–142 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.68 (m, 1H), 7.57 – 7.52 (m, 2H), 7.50 – 7.41 (m, 3H), 7.41 – 7.34 (m, 5H), 7.33 – 7.29 (m, 2H), 7.27 – 7.22 (m, 3H), 7.21 – 7.11 (m, 3H), 7.10 – 7.03 (m, 1H), 6.92 – 6.78 (m, 4H), 4.66 (d, *J* = 27.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.4, 140.0, 136.1, 134.9 (d, *J* = 4.4 Hz), 133.7 (d, *J* = 4.7 Hz), 133.1 (d, *J* = 9.3 Hz), 132.7, 130.9 (d, *J* = 5.3 Hz), 130.4 (d, *J* = 7.2 Hz), 129.3, 129.2, 129.1, 129.0 (d, *J* = 7.3 Hz), 128.8 (d, *J* = 3.9 Hz), 128.7, 128.6, 128.5, 128.4, 128.1, 127.8, 127.5, 127.1, 75.9 (d, *J* = 6.6 Hz), 49.9 (d, *J* = 79.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.28. HRMS (ESI) calcd for $C_{32}H_{26}O_2P^+$ $[M+H]^+$ *m/z*: 473.1665; found 473.1664.

Conflicts of interest

There are no conflicts of interest to declare.

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