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Cyclic α-Alkoxyphosphonium Salts from (2-(Diphenylphosphino)phenyl)methanol and Aldehydes and Their Application in Synthesis of Vinyl Ethers and Ketones via Wittig Olefination

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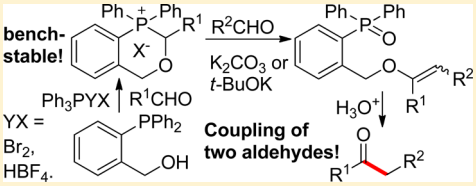
Supporting Information

ABSTRACT: Cyclic α-alkoxyphosphonium salts have been synthesized from (2-(diphenylphosphino)phenyl)methanol and aldehydes in 36−89% yields. These phosphonium salts are bench-stable solids and undergo Wittig olefination with aldehydes under basic conditions (K_2CO_3 or *t*-BuOK) to form benzylic vinyl ethers, which are readily hydrolyzed to 1,2-disubstituted ethanones under acidic conditions. The formation mechanism of these phosphonium salts via hemiacetal is also proposed.

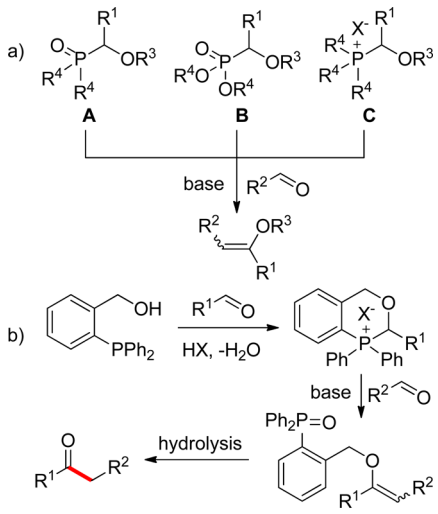


INTRODUCTION

Vinyl ethers have been widely used in not only organic synthesis[1−7] but also polymer synthesis[8] due to their electron-rich double bonds. Although a wide variety of methods are available for the synthesis of vinyl ethers, each method has its advantage and disadvantage with regard to reaction condition, stereoselectivity, and availability of starting materials.[9] Among these methods, the Wittig-type olefination of an aldehyde with an α-alkoxyphosphine oxide (**A**)[10,11] or α-alkoxyphosphonate (**B**)[12−18] or α-alkoxyphosphonium salt (**C**)[19−31] under basic conditions (Scheme 1a) seems to be an attractive way to access functionalized vinyl ethers. **A** is usually prepared from the hydrolysis of phosphonium salts[22] or the reaction of chlorodiphenylphosphine with acetal[32] or the reaction of diphenylphosphine with aldehyde and alcohol, followed by oxidation.[33] Four reactions have been utilized to prepare **B**: (1) chlorophosphite with acetal,[12] (2) dimethyl phosphite with aldehydes, followed by alkylation,[16] (3) trialkyl phosphite with acetal in the presence of a Lewis acid such as trimethylsilyl chloride[17] and $TiCl_4$,[18] and (4) dialkyl phosphonate and acetal in the presence of BF_3.[34] The preparation of C is often through the reactions of triphenyl- or trialkylphosphine with α-halo ethers[23,29,35] or acetals[20,24−28,36−39] or enol ethers.[22,40] The existing Wittig olefination using **A**−**C** presents several limitations: (1) The use of a strong base such as LDA, LHDMS, and NaH to generate the ylides or alkyl phosphonate carbanions makes it difficult to scale up. (2) The preformation of acetals from aldehydes reduces the efficiency of Wittig olefination for synthesis of vinyl ethers. (3) Some α-alkoxyphosphonium salts (in particular, when $R^1 \neq H$ for **C** in Scheme 1a) are unstable and water-sensitive,[19,23] and the generation of the corresponding ylides from (α-methoxyalkyl)-triphenylphosphonium salts requires low temperature (< −40 °C).[20]

To overcome these limitations, we hypothesized that a cyclic α-alkoxyphosphonium salt from the reaction of (2-(diphenyl-phosphino)phenyl)methanol (DPPPM) with an aldehyde should be more stable than the acyclic ones, and thus a weaker base might be used for subsequent Wittig olefination that should produce a benzylic vinyl ether and, after further hydrolysis, a ketone (Scheme 1b). Overall, this reaction sequence would also provide a more straightforward route to couple two aldehydes (R^1CHO and R^2CHO) to produce a ketone $R^1COCH_2R^2$ than the similar route using the acyclic α-

Scheme 1. Synthesis of Vinyl Ethers, Ketones via Wittig-Type Reactions



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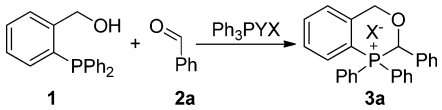
alkoxyphosphonium salts prepared from acetals. Herein, we report our experimental results on testing this hypothesis.

RESULTS AND DISCUSSION

DPPPM **1** was readily prepared[41] from the commercially available (2-diphenylphosphino)benzaldehyde by the reduction using $NaBH_4$. It has been applied in stereoselective Wittig olefination as a surrogate for triphenylphosphine.[42] When a solution of DPPPM **1** and an equimolar amount of benzaldehyde **2a** in THF were mixed with a nearly saturated solution of Ph_3PHBr in THF, white solids precipitated after the mixture was stirred at room temperature overnight. The white solids collected by filtration were identified as the desired phosphonium salt **3aa** by NMR spectra and HRMS, though its yield was only 24% (Table 1, entry 1). Refluxing the reaction

Table 1. Initial Observations on the Formation of Cyclic α-Alkoxyphosphonium Salts from DPPPM and Aldehydes



1 **2a** **3a**

entry	YX	Method[a]	3a	yield (%)
1	HBr	A	**3aa**	24
2	HBr	A[b]	**3aa**	25
3	HBr	A	**3aa**	17[c]
4	Br_2	A	**3aa**	49
5	HBF_4	A	**3ab**	64
6	Br_2	B[d]	**3aa**	74
7	Br_2	B[e]	**3aa**	78
8	HBF_4	B[e]	**3ab**	74

[a]Method A: mixed a solution of **1** (0.86 mmol) and **2** (0.86 mmol) in 2 mL of THF with a saturated solution of Ph_3PYX in THF (12 mL for Ph_3PHBr, 5 mL for Ph_3HBF_4 and Ph_3PBr_2), rt, overnight. Method B: mixed **1**, **2**, and Ph_3PYX with a certain amount of THF, rt, overnight. [b]Refluxing for 9 h. [c]Using 2 equiv of Ph_3PHBr in THF (26 mL). [d]Using 4 mL of THF. [e]Using 1 mL of THF.

mixture for 9 h led to the almost same yield (entry 2). Increasing the usage of Ph_3PHBr to 2 equiv reduced the yield of **3aa** to 17% (entry 3). The yield of **3aa** could be improved to 49% when using Ph_3PBr_2 instead of Ph_3PHBr (entry 4). Further switching to Ph_3PHBF_4 afforded **3ab** in 64% yield (entry 5). Interestingly, the yield of **3aa** was dramatically increased to 74% by simply reducing the usage of THF (entry 6). Further reducing the usage of THF, **3aa** and **3ab** were obtained in 78% and 74% yields, respectively (entries 7 and 8).

We next examined a variety of aldehydes (Figure 1, **2a**–**2q**) for the formation of phosphonium salts **3**, and the results are summarized in Table 2. In general, electron-rich aromatic aldehydes gave higher yields of **3** than electron-deficient ones, except for *p*-fluorobenzaldehyde, which, surprisingly, gave **3f** in the highest yield (89%, entry 8). *o*-Nitrobenzaldehyde **2e** gave a lower yield than *p*-nitrobenzaldehyde **2d** and *m*-nitrobenzaldehyde **2f**, possibly due to the steric effect of the *ortho* nitro group (entries 5–7). The same ortho-steric effect was observed for chlorobenzaldehyde (entries 3–4). Heteroaromatic 2-furaldehyde and aliphatic isobutyraldehyde provided **3qa** and **3pa** in moderate yields (entries 17–18). It is noteworthy that these phosphonium salts are all bench-stable solids and can be weighed in air without special considerations. In addition, the

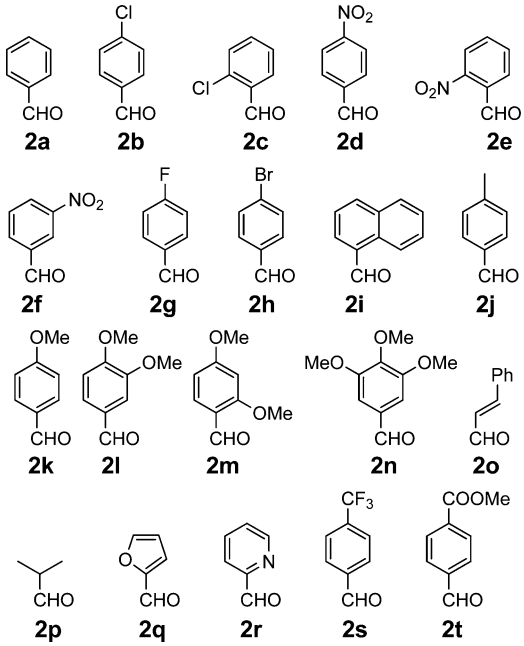
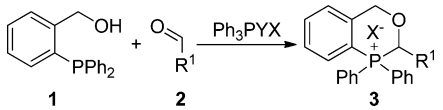


Figure 1. Aldehydes used in this work.

Table 2. Synthesis of Cyclic α-Alkoxyphosphonium Salts from DPPPM and Aldehydes



1 **2** **3**

entry	YX	R^1	3	yield[a] (%)
1	Br_2	Ph	**3aa**	78
2	HBF_4	Ph	**3ab**	74
3	Br_2	4-ClC_6H_4	**3ba**	68
4	Br_2	2-ClC_6H_4	**3ca**	57
5	Br_2	4-$O_2NC_6H_4$	**3da**	50
6	Br_2	2-$O_2NC_6H_4$	**3ea**	36
7	Br_2	3-$O_2NC_6H_4$	**3fa**	53
8	Br_2	4-FC_6H_4	**3ga**	89
9	HBF_4	4-BrC_6H_4	**3hb**	73
10	HBF_4	1-naphthyl	**3ib**	75
11	HBF_4	4-MeC_6H_4	**3jb**	86
12	HBF_4	4-$MeOC_6H_4$	**3kb**	81
13	HBF_4	3,4-$(MeO)_2C_6H_3$	**3 lb**	89
14	HBF_4	2,4-$(MeO)_2C_6H_3$	**3mb**	84
15	HBF_4	3,4,5-$(MeO)_2C_6H_2$	**3nb**	82
16	HBF_4	(*E*)-PhCH=CH	**3ob**	87
17	Br_2	*i*-Pr	**3pa**	63
18	Br_2	2-furyl	**3qa**	64

[a]Reaction conditions: **1** (0.7 mmol), **2** (0.70 mmol), Ph_3PBr_2 (0.38 mmol) or Ph_3PHBF_4 (0.70 mmol), THF (1 mL), rt, overnight.

preparation of **3** can be easily run on a large scale (20 mmol; see the Experimental Section).

With cyclic α-alkoxyphosphonium salts **3** in hand, we began to explore the possibility of their application in Wittig olefination with aldehydes, and the results are revealed in Table 3. Initially, we examined the reaction of phosphonium salt **3aa** with a variety of aldehydes using K_2CO_3 as a base. When a mixture of phosphonium salt **3aa**, aldehyde **2b**, and K_2CO_3 in $DMSO/CH_3CN$ (5/1) was stirred at room temperature overnight, **4ab** was isolated as an inseparable *Z*/

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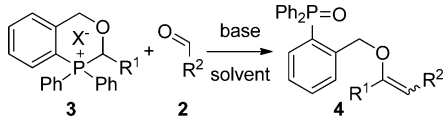
Table 3. Synthesis of Vinyl Ethers Using Cyclic α-Alkoxyphosphonium Salts



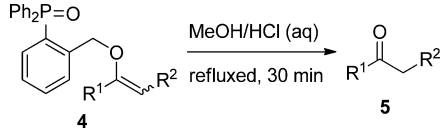
entry	A/B[a]	R^1	R^2	4	yield (%)[b]
1	A	Ph	4-ClC_6H_4	**4ab**	61 (89:11)
2	A	Ph	4-$O_2NC_6H_4$	**4ad**	84 (85:15)
3	A	Ph	2-$O_2NC_6H_4$	**4ae**	75 (40:60)
4	A	Ph	4-BrC_6H_4	**4ah**	70 (89:11)
5	A	Ph	(*E*)-PhCH=CH	**4ao**	45 (93:7)
6	A	Ph	2-furyl	**4aq**	80 (94:6)
7	A	Ph	2-pyridyl	**4ar**	61 (44:56)[c]
8	A	4-BrC_6H_4	4-FC_6H_4	**4hg**	80 (89:11)
9	A	4-FC_6H_4	4-$O_2NC_6H_4$	**4gd**	68 (95:5)
10	A	2-Furyl	4-$F_3CC_6H_4$	**4qs**	96 (85:15)
11	A	4-MeC_6H_4	4-$MeO_2CC_6H_4$	**4jt**	87 (93:7)
12	A	(*E*)-PhCH=CH	4-$O_2NC_6H_4$	**4od**	80 (48:52)
13	A	3,4,5-$(MeO)_3C_6H_2$	4-$O_2NC_6H_4$	**4nd**	84 (79:21)
14	A	Ph	Ph	**4aa**	19 (90:10)
15	A	Ph	4-MeC_6H_4	**4aj**	20 (93:7)
16	A	Ph	3,4-$(MeO)_2C_6H_3$	**4al**	[d]
17	B	Ph	Ph	**4aa**	85 (95:5)
18	B	Ph	4-MeC_6H_4	**4aj**	87 (96:4)
19	B	Ph	4-$MeOC_6H_4$	**4ak**	87 (97:3)
20	B	Ph	3,4-$(MeO)_2C_6H_3$	**4al**	81 (93:7)
21	B	3,4,5-$(MeO)_3C_6H_2$	4-$MeOC_6H_4$	**4nk**	68 (91:9)
22	B	Ph	*i*-Pr	**4ap**	28[e] (93:7)

[a]Condition A: **2** (0.31 mmol), **3** (0.37 mmol), K_2CO_3 (0.44 mmol), DMSO (1 mL), and CH_3CN (0.2 mL), rt, overnight. Condition B: **2** (0.25 mmol), **3** (0.25 mmol), anhyd THF (5 mL), *t*-BuOK in THF (1.0 M, 0.3 mL), rt, 3 h. [b]The number in the parentheses is the *Z*:*E* ratio determined by ^1H NMR. [c]Isolated *Z*:*E* ratio. [d]**4al** was not detected. [e]Using 1.2 equiv of **3aa**.

E mixture in 61% yield (entry 1). Other aldehydes including electron-deficient aromatic aldehydes, cinnamyl aldehyde, and two heteroaromatic aldehydes underwent olefination to give the corresponding vinyl ethers in moderate to good yields (entries 2−7). A number of combinations of phosphonium salts **3** and aldehydes **2** also gave the corresponding vinyl ethers in moderate to good yields (entries 8−13). The configuration of these vinyl ethers was determined by NOESY spectra, and in most of cases, the *Z*/*E* selectivity is in favor of the (*Z*)-isomer, in contrast to that reported[19] by Das and McNulty using the acyclic α-alkoxyphosphonium salts. It seems that the reaction depends on both the easiness of deprotonation of phosphonium salts **3** and the activity of the carbonyl group of aldehydes **2** toward the ylide. The deprotonation to form the ylide for phosphonium salts **3** formed from electron-deficient aromatic aldehydes is easier than those from electron-rich ones. Therefore, phosphonium salt **3** from an electron-rich aldehdye may react well with an electron-deficient aldehyde (entries 11 and 13). However, combinations of **3aa**−**2a** and **3aa**−**2j** led to the poor yields of **4aa** and **4aj** (entries 14 and 15). The combination of **3aa**−**2l** even did not produce the desired vinyl ether **4al** (entry 16). This is probably due to the superposition of the low efficiency of deprotonation of phosphonium salt **3** and the low activity of aldehyde **2**. Therefore, we switched to a stronger base (*t*-BuOK/THF) for the reactions of **3aa** with a number of electron-rich aldehydes, and the results showed that the corresponding vinyl ethers were obtained in high yields and with high *Z*/*E* ratios (entries 17−21). However, the reaction of **3aa** with aliphatic aldehyde **2p** led to a low yield of **4ap** (28%, entry 22), probably due to the enolization of **2p**. Attempts to synthesize vinyl ethers from **3pa** and **2a** or **2p** were unsuccessful.

We further explored the possibility for converting the obtained benzylic vinyl ethers **4** to the corresponding ketones. When a solution of vinyl ether **4aa** in MeOH:6 M HCl (3:1, v/v) was refluxed for 30 min, TLC showed that **4aa** was completely hydrolyzed and **5a** was obtained in 81% yield (Table 4, entry 1). Other vinyl ethers from a variety of combinations of phosphonium salt **3** and aldehydes **2** were readily hydrolyzed to ketones in good to nearly quantitative yields (entries 2−8). A one-pot synthesis of **5a** starting from **3aa** and **2a** was carried out on a gram scale to afford **5a** in 54% yield (see the Experimental Section for details). 1,2-Diary-

Table 4. Synthesis of Ketones by Hydrolysis of Vinyl Ethers



entry	R^1	R^2	5	yield (%)
1	Ph	Ph	**5a**	81
2	Ph	4-MeC_6H_4	**5b**	78
3	Ph	3,4-$(MeO)_2C_6H_3$	**5c**	85
4	(*E*)-PhCH=CH	4-$O_2NC_6H_4$	**5d**	73
5	3,4,5-$(MeO)_2C_6H_2$	4-$O_2NC_6H_4$	**5e**	86
6	4-MeC_6H_4	4-$MeO_2CC_6H_4$	**5f**	75
7	2-furyl	4-$F_3CC_6H_4$	**5g**	78
8	3,4,5-$(MeO)_2C_6H_2$	4-$MeOC_6H_4$	**5h**	98

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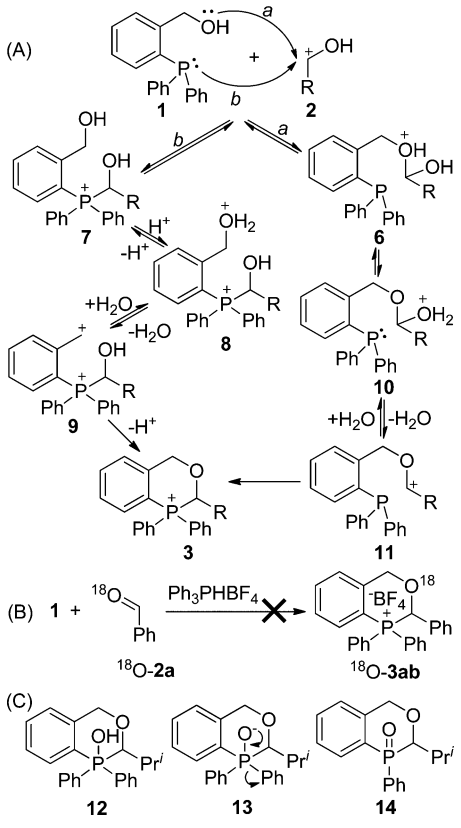
lethanones are useful building blocks for synthesizing a variety of heterocycles[43] and natural products.[44] 1,2-Diarylethanones can be synthesized by Friedel−Crafts acylation of electron-rich aromatic compounds with aryl acetic acids or chlorides,[45] by hydration of diarylethyne,[46] and by transition-metal-catalyzed carbonylative coupling reaction of benzyl halides with potassium aryltrifluorborates.[47] These methods either suffer from a lack of regioselectivity or require a noble metal. General methods for preparation of 1,2-diarylethanones from aromatic aldehydes including: (1) addition of benzylic Grignard reagents to aromatic aldehydes, followed by oxidation of the resulting secondary alcohols,[48] which suffers from low yields due to the coupling aptness of the benzylic Grignard reagent, (2) selective deoxygenation of benzoins,[49] which is limited to symmetrical benzoins, (3) transformation into carbonyl anion equivalent, followed by metalation, benzylation, and deprotection, which usually requires a strong base such as BuLi,[50] and (4) synthesis of vinyl ethers as described in Scheme 1a, followed by hydrolysis, drawbacks of which we have already analyzed in the Introduction. Our methodology for synthesis of 1,2-diarylethanones has the following advantages: (1) cyclic α-alkoxy phosphonium salts are readily prepared from aldehydes and bench-stable solids; (2) two aromatic aldehydes are used as starting materials, allowing various combinations of two aryl groups, including deficient-deficient, rich-rich, rich-deficient, and deficient-rich in the context of electron; and (3) mild reaction condition without using a strong base such as BuLi and LDA.

There are two possible pathways for the formation of phosphonium salts **3**, as shown in Scheme 2A. In path *a*, phosphine **1** reacts on oxygen with protonated aldehyde **2** (the proton may come from HBF_4 or HBr) to form hemiacetal **6**, which, after proton-exchange, loses a water and undergoes intramolecular nucleophilic substitution to produce phosphonium salt **3**. In path *b*, phosphine **1** reacts on phosphorus with protonated aldehyde **2** to form α-hydroxyphosphonium salt **7**, which, after protonation and intramolecular nucleophilic substitution via **8** and **9**, forms phosphonium salt **3**. To distinguish these two pathways, we conducted an ^{18}O-labeling experiment in which ^{18}O-**2a** and **1** were treated with Ph_3PHBF_4 according to the same procedure to prepare **3ab**. The resulting phosphonium salt was analyzed by NMR and HRMS, and none of them showed the formation of phosphonium salt ^{18}O-**3ab** (Scheme 2B). Therefore, the path *b* via the intermediates **7**−**9** could be excluded. As for the reactions of **3pa** with **2a** and **2p** in the presence of *t*-BuOK, a cyclic phosphine oxide **14** (Scheme 2C) was isolated in 81% and 96% yields, respectively, and is a mixture of two stereoisomers with ratios of 79:21 and 68:32, respectively. We reasoned that **14** might form from **3pa** via nucleophilic attack to phosphorus by $^-$OH, which might be generated in situ from the reaction of *t*-BuOK with a trace of water, to produce **12**, followed by base-promoted fragmentation via **13** to lose a phenyl group. Phosphonium salts formed from aromatic aldehydes have no such problem, which might be due to the stronger acidity of their α-Hs than that of **3pa**, leading the easier formation of their ylides than that of **3pa**. Alkyltriphenylphosphonium salts have been reported[51] to lose a phenyl group to form alkyldiphenylphosphine oxide in the presence of *t*-BuOK or NaH. In addition, the hydrolysis of alkyltriphenylphosponium salts under basic conditions has also been used to prepare[22] alkyldiphenylphosphine oxide.

Scheme 2. Formation Mechanism of Cyclic α-Alkoxyphosphonium Salts



CONCLUSION

In summary, we have synthesized a variety of cylclic α-alkoxyphosphonium salts from DPPPM and aldehydes. These phosphonium salts are bench-stable solids and can undergo Wittig olefination with aromatic aldehydes to provide benzylic vinyl ethers with the Z/*E* selectivities mostly favoring the (*Z*)-isomer under mild conditions. Furthermore, these vinyl ethers are readily hydrolyzed to the corresponding ketones. Therefore, this methodology provides a facile way to couple two aldehydes to form 1,2-diarylethanones.

EXPERIMENTAL SECTION

General. All solvents were freshly distilled before use. All aldehydes were purified by preparative TLC before use. The olefination reactions were performed under nitrogen by connecting the flask to a nitrogen balloon. The melting points were measured on a melting apparatus with a microscope and hot stage and were uncorrected. PE = petroleum ether (bp 60−90 °C).

General Procedure for Synthesis of Cyclic α-Alkoxyphosphonium Salts. To a test tube (10 mL) were added DPPPM **1** (204.5 mg, 0.70 mmol), Ph_3PBr_2 (162.5 mg, 0.38 mmol) or Ph_3PHBF_4 (245.1 mg, 0.70 mmol), aldehyde **2** (0.70 mmol), and THF (1 mL). After they were stirred at rt overnight, the resulting precipitates were collected by filtration and dried in vacuo to give phosphonium salt **3**.

*1,1,2-Triphenyl-2,4-dihydro-1H-benzo[d][1,3]oxaphosphinin-1-ium Bromide (**3aa**).* A white solid, yield: 250.6 mg, 78%; mp: 217−218 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 5.57 (d, 1 H, J = 16.2 Hz), 5.68 (d, 1 H, J = 16.2 Hz), 6.91 (d, 2 H, J = 8.2 Hz), 6.95 (dd, 2 H, J_1 = 8.0 Hz, $J_{2C\text{-}P}$ = 12.4 Hz), 7.30 (dd, 2 H, J_1 = 7.6 Hz, J_2 = 8.2 Hz), 7.40 (dd, 1 H, $J_{1C\text{-}P}$ = 6.8 Hz, J_2 = 7.2 Hz), 7.53 (d, 1 H, $J_{C\text{-}P}$ = 3.2 Hz), 7.56−7.67 (m, 4 H), 7.75 (dd, 1 H, $J_{1C\text{-}P}$ = 6.4 Hz, J_2 = 6.4 Hz), 7.80−7.92 (m, 3 H), 7.92−8.04 (m, 2 H), 8.23 (dd, 2 H, J_1 = 8.0 Hz, $J_{2C\text{-}P}$ = 12.0 Hz). ^{13}C NMR (151 MHz, DMSO-d_6) δ 70.6, 74.4 (d, $J_{C\text{-}P}$ = 55.6 Hz), 112.9 (d, $J_{C\text{-}P}$ = 80.5 Hz), 113.8 (d, $J_{C\text{-}P}$ = 84.7 Hz), 116.0 (d, $J_{C\text{-}P}$

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= 79.3 Hz), 126.1 (d, $J_{C\text{-}P}$ = 4.5 Hz), 126.6 (d, $J_{C\text{-}P}$ = 8.6 Hz), 128.7 (d, $J_{C\text{-}P}$ = 2.1 Hz), 129.1 (d, $J_{C\text{-}P}$ = 11.6 Hz), 129.607, 129.609 (d, $J_{C\text{-}P}$ = 12.4 Hz), 130.5 (d, $J_{C\text{-}P}$ = 12.4 Hz), 131.0 (d, $J_{C\text{-}P}$ = 2.1 Hz), 134.2 (d, $J_{C\text{-}P}$ = 6.6 Hz), 134.8 (d, $J_{C\text{-}P}$ = 10.0 Hz), 135.1 (d, $J_{C\text{-}P}$ = 9.5 Hz), 135.2, 135.5, 135.8 (d, $J_{C\text{-}P}$ = 2.0 Hz), 143.1 (d, $J_{C\text{-}P}$ = 3.6 Hz). ^{31}P NMR (162 MHz, DMSO-d_6) δ 2.85. HRMS (MALDI-TOF) m/z [M − Br^-] Calcd for $C_{26}H_{22}OP^+$ 381.1403; Found 381.1405. The preparation of **3aa** was also scaled up using DPPPM (20 mmol), aldehyde **2a** (20 mmol), Ph_3PBr_2 (11 mmol), and THF (28 mL), and **3aa** was obtained in 96% (8.72 g) yield.

*1,1,2-Triphenyl-2,4-dihydro-1H-benzo[d][1,3]oxaphosphinin-1-ium Tetrafluoroborate (**3ab**).* A white solid, yield: 242.1 mg, 74%; mp: 235−236 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 5.56 (d, 1 H, J = 16.4 Hz), 5.60 (d, 1 H, J = 16.4 Hz), 6.90 (d, 2 H, J = 7.6 Hz), 6.96 (dd, 2 H, J_1 = 7.8 Hz, $J_{2C\text{-}P}$ = 12.2 Hz), 7.27−7.33 (m, 3 H), 7.37−7.43 (m, 1 H), 7.55−7.67 (m, 4 H), 7.71−7.77 (m, 1 H), 7.81−7.91 (m, 3 H), 7.91−8.02 (m, 2 H), 8.17 (dd, 2 H, J_1 = 7.6 Hz, $J_{2C\text{-}P}$ = 12.4 Hz). ^{13}C NMR (100 MHz, DMSO-d_6) δ 71.3, 75.3 (d, $J_{C\text{-}P}$ = 55.1 Hz), 113.3 (d, $J_{C\text{-}P}$ = 80.1 Hz), 114.2 (d, $J_{C\text{-}P}$ = 84.4 Hz), 116.5 (d, $J_{C\text{-}P}$ = 78.7 Hz), 126.6 (d, $J_{C\text{-}P}$ = 4.4 Hz), 127.0 (d, $J_{C\text{-}P}$ = 8.6 Hz), 129.2 (d, $J_{C\text{-}P}$ = 2.9 Hz), 129.7 (d, $J_{C\text{-}P}$ = 11.9 Hz), 130.1 (d, $J_{C\text{-}P}$ = 12.5 Hz), 130.2, 131.1 (d, $J_{C\text{-}P}$ = 12.3 Hz), 131.3 (d, $J_{C\text{-}P}$ = 2.5 Hz), 134.6 (d, $J_{C\text{-}P}$ = 6.7 Hz), 135.1 (d, $J_{C\text{-}P}$ = 9.7 Hz), 135.6 (d, $J_{C\text{-}P}$ = 9.4 Hz), 135.7, 136.0 (d, $J_{C\text{-}P}$ = 2.5 Hz), 136.3 (d, $J_{C\text{-}P}$ = 2.5 Hz), 143.5 (d, $J_{C\text{-}P}$ = 3.7 Hz). ^{31}P NMR (162 MHz, DMSO-d_6) δ 2.81. ^{11}B-NMR (128 MHz, DMSO-d_6) δ −1.20. ^{19}F-NMR (376 MHz, DMSO-d_6) δ −148.3, −148.2. HRMS (MALDI-TOF) m/z [M − F_4B^-] Calcd for $C_{26}H_{22}OP^+$ 381.1403; Found 381.1406.

*2-(4-Chlorophenyl)-1,1-diphenyl-2,4-dihydro-1H-benzo[d][1,3]-oxaphosphinin-1-ium Bromide (**3ba**).* A white solid, yield: 236.0 mg, 68%; mp: 236−237 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 5.55 (dd, 1 H, J_1 = 2.2 Hz, J_2 = 16.4 Hz), 5.61 (d, 1 H, J = 16.4 Hz), 6.89 (dd, 2 H, $J_{1C\text{-}P}$ = 2.2 Hz, J_2 = 8.5 Hz), 7.01 (dd, 2 H, J_1 = 7.8 Hz, $J_{2C\text{-}P}$ = 12.6 Hz), 7.39 (d, 2 H, J_2 = 8.5 Hz), 7.45 (d, 1 H, $J_{C\text{-}P}$ = 3.6 Hz), 7.56−7.67 (m, 4 H), 7.70−7.75 (m, 1 H), 7.80−7.86 (m, 2 H), 7.87−7.95 (m, 2 H), 7.96−8.01 (m, 1 H), 8.20 (dd, 2 H, J_1 = 8.0 Hz, $J_{2C\text{-}P}$ = 12.4 Hz). ^{13}C NMR (100 MHz, DMSO-d_6) δ 71.2 (d, $J_{C\text{-}P}$ = 1.8 Hz), 74.2 (d, $J_{C\text{-}P}$ = 54.8 Hz), 113.3 (d, $J_{C\text{-}P}$ = 80.4 Hz), 114.2 (d, $J_{C\text{-}P}$ = 83.8 Hz), 116.2 (d, $J_{C\text{-}P}$ = 78.9 Hz), 127.1 (d, $J_{C\text{-}P}$ = 8.8 Hz), 128.5 (d, $J_{C\text{-}P}$ = 4.6 Hz), 129.3 (d, $J_{C\text{-}P}$ = 2.0 Hz), 129.7 (d, $J_{C\text{-}P}$ = 11.9 Hz), 130.3 (d, $J_{C\text{-}P}$ = 12.5 Hz), 130.5 (d, $J_{C\text{-}P}$ = 2.5 Hz), 131.1 (d, $J_{C\text{-}P}$ = 12.4 Hz), 134.5 (d, $J_{C\text{-}P}$ = 6.5 Hz), 134.8 (d, $J_{C\text{-}P}$ = 4.1 Hz), 135.4 (d, $J_{C\text{-}P}$ = 10.0 Hz), 135.66 (d, $J_{C\text{-}P}$ = 9.9 Hz), 135.71, 136.1 (d, $J_{C\text{-}P}$ = 2.2 Hz), 136.4 (d, $J_{C\text{-}P}$ = 2.6 Hz), 143.5 (d, $J_{C\text{-}P}$ = 3.6 Hz). ^{31}P NMR (162 MHz, DMSO-d_6) δ 3.21. HRMS (MALDI-TOF) m/z [M − Br^-] Calcd for $C_{26}H_{21}ClOP^+$ 415.1013; Found 415.1012.

*2-(2-Chlorophenyl)-1,1-diphenyl-2,4-dihydro-1H-benzo[d][1,3]-oxaphosphinin-1-ium Bromide (**3ca**).* A white solid, yield: 198.2 mg, 57%; mp: 258−260 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 5.51 (dd, 1 H, J_1 = 2.0 Hz, J_2 = 16.0 Hz), 5.89 (d, 1 H, J = 16.0 Hz), 6.66 (dd, 1 H, $J_{1C\text{-}P}$ = 8.0 Hz), 7.05−7.16 (m, 3 H), 7.39−7.42 (m, 1 H), 7.46−7.57 (m, 3 H), 7.58−7.66 (m, 3 H), 7.71−7.79 (m, 3 H), 7.87−7.95 (m, 3 H), 8.17 (dd, 2 H, J_1 = 8.0 Hz, $J_{2C\text{-}P}$ = 12.8 Hz). ^{13}C NMR (151 MHz, DMSO-d_6) δ 70.1, 73.7 (d, $J_{C\text{-}P}$ = 55.1 Hz), 112.95 (d, $J_{C\text{-}P}$ = 83.2 Hz), 113.02 (d, $J_{C\text{-}P}$ = 81.8 Hz), 116.4 (d, $J_{C\text{-}P}$ = 78.2 Hz), 126.5 (d, $J_{C\text{-}P}$ = 8.6 Hz), 127.3 (d, $J_{C\text{-}P}$ = 2.6 Hz), 129.2 (d, $J_{C\text{-}P}$ = 12.2 Hz), 129.5 (d, $J_{C\text{-}P}$ = 2.1 Hz), 129.6 (d, $J_{C\text{-}P}$ = 3.8 Hz), 129.8 (d, $J_{C\text{-}P}$ = 12.7 Hz), 129.9 (d, $J_{C\text{-}P}$ = 1.5 Hz), 130.0 (d, $J_{C\text{-}P}$ = 12.7 Hz), 130.5 (d, $J_{C\text{-}P}$ = 5.6 Hz), 131.5 (d, $J_{C\text{-}P}$ = 3.3 Hz), 134.4 (d, $J_{C\text{-}P}$ = 7.1 Hz), 135.1 (d, $J_{C\text{-}P}$ = 10.3 Hz), 135.2, 135.3 (d, $J_{C\text{-}P}$ = 9.5 Hz), 135.57, 135.58, 143.6 (d, $J_{C\text{-}P}$ = 3.5 Hz). ^{31}P NMR (162 MHz, DMSO-d_6) δ 3.11. HRMS (MALDI-TOF) m/z [M − Br^-] Calcd for $C_{26}H_{21}ClOP^+$ 415.1013; Found 415.1014.

*2-(4-Nitrophenyl)-1,1-diphenyl-2,4-dihydro-1H-benzo[d][1,3]-oxaphosphinin-1-ium Bromide (**3da**).* A pale yellow solid, yield: 177.2 mg, 50%; mp: 176−178 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 5.59 (dd, 1 H, $J_{1C\text{-}P}$ = 2.2 Hz, J_2 = 16.5 Hz), 5.66 (d, 1 H, $J_{C\text{-}P}$ = 16.5 Hz), 6.99 (d, 2 H, J_1 = 7.6 Hz, $J_{2C\text{-}P}$ = 12.4 Hz), 7.15 (d, 2 H, $J_{1C\text{-}P}$ = 2.0 Hz, J_2 = 8.8 Hz), 7.56−7.65 (m, 4 H), 7.69 (s, 1 H), 7.75 (dd, 1 H, $J_{1C\text{-}P}$ = 6.4 Hz, J_2 = 7.2 Hz), 7.82−7.91 (m, 3 H), 7.95 (dd, 1 H, $J_{1C\text{-}P}$ = 7.6 Hz, J_2 = 8.4 Hz), 8.00 (dd, 1 H, $J_{1C\text{-}P}$ = 6.8 Hz, J_2 = 8.0 Hz), 8.16 (d, 2 H, J = 8.4 Hz), 8.22 (dd, 2 H, J_1 = 7.8 Hz, $J_{2C\text{-}P}$ = 12.6 Hz). ^{13}C NMR (100 MHz, DMSO-d_6) δ 71.2, 74.3 (d, $J_{C\text{-}P}$ = 55.5 Hz), 113.0 (d, $J_{C\text{-}P}$ = 81.8 Hz), 113.8 (d, $J_{C\text{-}P}$ = 84.4 Hz), 115.9 (d, $J_{C\text{-}P}$ = 79.4 Hz), 124.4, 127.2 (d, $J_{C\text{-}P}$ = 9.1 Hz), 128.0, 129.8 (d, $J_{C\text{-}P}$ = 11.7 Hz), 130.4 (d, $J_{C\text{-}P}$ = 12.1 Hz), 131.2 (d, $J_{C\text{-}P}$ =12.2 Hz), 134.6 (d, $J_{C\text{-}P}$ = 6.0 Hz), 135.6 (d, $J_{C\text{-}P}$ = 11.3 Hz), 135.7 (d, $J_{C\text{-}P}$ = 10.4 Hz), 135.9, 136.3, 136.6, 138.7, 143.4, 148.5. ^{31}P NMR (162 MHz, DMSO-d_6) δ 4.18. HRMS (MALDI-TOF) m/z [M − Br^-] Calcd for $C_{26}H_{21}NO_3P^+$ 426.1254; Found 426.1252.

*2-(2-Nitrophenyl)-1,1-diphenyl-2,4-dihydro-1H-benzo[d][1,3]-oxaphosphinin-1-ium Bromide (**3ea**).* A pale yellow solid, yield: 127.4 mg, 36%; mp: 260−262 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 5.51 (dd, 1 H, $J_{1C\text{-}P}$ = 2.0 Hz, J_2 = 16.0 Hz), 5.72 (d, 1 H, $J_{C\text{-}P}$ = 16.0 Hz), 7.10 (d, 1 H, $J_{C\text{-}P}$ = 7.6 Hz), 7.18 (d, 2 H, J_1 = 7.6 Hz, $J_{2C\text{-}P}$ = 12.4 Hz), 7.50−7.68 (m, 6 H), 7.71−7.79 (m, 4 H), 7.84 (dd, 1 H, $J_{1C\text{-}P}$ = 7.2 Hz, J_2 = 7.6 Hz), 7.87−7.94 (m, 2 H), 8.00 (dd, 1 H, J = 8.0 Hz), 8.11 (dd, 2 H, J_1 = 7.6 Hz, $J_{2C\text{-}P}$ = 12.8 Hz). ^{13}C NMR (100 MHz, DMSO-d_6) δ 70.7 (d, $J_{C\text{-}P}$ = 3.8 Hz), 74.2 (d, $J_{C\text{-}P}$ = 52.7 Hz), 113.6 (d, $J_{C\text{-}P}$ = 56.3 Hz), 114.5 (d, $J_{C\text{-}P}$ = 57.4 Hz), 117.9 (d, $J_{C\text{-}P}$ = 79.0 Hz), 125.6 (d, $J_{C\text{-}P}$ = 2.0 Hz), 127.33 (d, $J_{C\text{-}P}$ = 1.6 Hz), 127.34 (d, $J_{C\text{-}P}$ = 8.4 Hz), 129.87 (d, $J_{C\text{-}P}$ = 11.9 Hz), 129.90 (d, J = 4.7 Hz), 130.3 (d, $J_{C\text{-}P}$ = 12.7 Hz), 130.5 (d, $J_{C\text{-}P}$ = 12.7 Hz), 131.5 (d, $J_{C\text{-}P}$ = 2.9 Hz), 134.5 (d, $J_{C\text{-}P}$ = 2.7 Hz), 134.8 (d, $J_{C\text{-}P}$ = 4.8 Hz), 134.9 (d, $J_{C\text{-}P}$ = 10.1 Hz), 135.55, 135.60 (d, $J_{C\text{-}P}$ = 9.6 Hz Hz), 135.7 (d, $J_{C\text{-}P}$ = 3.0 Hz), 136.0 (d, $J_{C\text{-}P}$ = 2.9 Hz), 144.0 (d, $J_{C\text{-}P}$ = 3.6 Hz), 146.9 (d, $J_{C\text{-}P}$ = 5.2 Hz). ^{31}P NMR (243 MHz, DMSO-d_6) δ 4.96. HRMS (MALDI-TOF) m/z [M − Br^-] Calcd for $C_{26}H_{21}NO_3P^+$ 426.1254; Found 426.1260.

*2-(3-Nitrophenyl)-1,1-diphenyl-2,4-dihydro-1H-benzo[d][1,3]-oxaphosphinin-1-ium Bromide (**3fa**).* A white solid, yield: 189.1 mg, 53%; mp: 159−161 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 5.60 (dd, 1 H, $J_{1C\text{-}P}$ = 2.0 Hz, J_2 = 16.4 Hz), 5.86 (d, 1 H, $J_{C\text{-}P}$ = 16.4 Hz), 7.01 (d, 2 H, J_1 = 7.8 Hz, $J_{2C\text{-}P}$ = 12.2 Hz), 7.45−7.50 (m, 2 H), 7.56−7.66 (m, 5 H), 7.77 (dd, 1 H, $J_{1C\text{-}P}$ = 6.4 Hz, J_2 = 6.8 Hz), 7.80−7.90 (m, 3 H), 7.90−7.95 (m, 1 H), 7.99 (dd, 1 H, $J_{1C\text{-}P}$ = 7.2 Hz, J_2 = 7.2 Hz), 8.22 (d, 1 H, J = 8.0 Hz), 8.29 (s, 1 H), 8.42 (dd, 2 H, J_1 = 8.0 Hz, $J_{2C\text{-}P}$ = 12.0 Hz). ^{13}C NMR (100 MHz, DMSO-d_6) δ 71.2, 73.7 (d, $J_{C\text{-}P}$ = 55.0 Hz), 112.9 (d, $J_{C\text{-}P}$ = 81.3 Hz), 114.0 (d, $J_{C\text{-}P}$ = 83.7 Hz), 115.6 (d, $J_{C\text{-}P}$ = 79.2 Hz), 121.4 (d, $J_{C\text{-}P}$ = 4.4 Hz), 124.9 (d, $J_{C\text{-}P}$ = 2.9 Hz), 127.1 (d, $J_{C\text{-}P}$ = 8.7 Hz), 129.7 (d, $J_{C\text{-}P}$ = 12.1 Hz), 130.3 (d, $J_{C\text{-}P}$ = 12.6 Hz), 131.1 (overlapped), 131.2 (d, $J_{C\text{-}P}$ = 12.4 Hz), 133.1 (d, $J_{C\text{-}P}$ = 4.2 Hz), 133.6 (d, $J_{C\text{-}P}$ = 2.2 Hz), 134.5 (d, $J_{C\text{-}P}$ = 7.0 Hz), 135.5 (d, $J_{C\text{-}P}$ = 10.1 Hz), 135.7 (d, $J_{C\text{-}P}$ = 9.6 Hz), 135.8 (d, $J_{C\text{-}P}$ = 1.7 Hz), 136.2 (d, $J_{C\text{-}P}$ = 2.6 Hz), 136.5 (d, $J_{C\text{-}P}$ = 2.3 Hz), 143.4 (d, $J_{C\text{-}P}$ = 3.6 Hz), 147.9 (d, $J_{C\text{-}P}$ = 3.3 Hz). ^{31}P NMR (162 MHz, DMSO-d_6) δ 4.06. HRMS (MALDI-TOF) m/z [M − Br^-] Calcd for $C_{26}H_{21}NO_3P^+$ 426.1254; Found 426.1255.

*2-(4-Fluorophenyl)-1,1-diphenyl-2,4-dihydro-1H-benzo[d][1,3]-oxaphosphinin-1-ium Bromide (**3ga**).* A white solid, yield: 297.1 mg, 89%; mp: 216−218 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 5.54 (dd, 1 H, $J_{1C\text{-}P}$ = 2.0 Hz, J_2 = 16.3 Hz), 5.72 (dd, 1 H, $J_{1C\text{-}P}$ = 5.0 Hz, J_2 = 16.3 Hz), 6.90−7.02 (m, 4 H), 7.15 (d, 2 H, J_1 = 8.6 Hz, J_2 = 8.6 Hz), 7.55−7.67 (m, 4 H), 7.70−7.77 (m, 2 H), 7.78−7.85 (m, 2 H), 7.86−8.00 (m, 3 H), 8.24−8.32 (m, 2 H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 71.2, 74.4 (d, $J_{C\text{-}P}$ = 55.7 Hz), 113.3 (d, $J_{C\text{-}P}$ = 80.1 Hz), 114.2 (d, $J_{C\text{-}P}$ = 84.0 Hz), 116.27 (d, $J_{C\text{-}P}$ = 79.0 Hz), 116.33 (d, $J_{1C\text{-}P}$ = 2.4 Hz, $J_{2C\text{-}F}$ = 22.0 Hz), 127.1 (d, $J_{C\text{-}P}$ = 8.8 Hz), 127.7, 129.0 (dd, $J_{1C\text{-}P}$ = 4.7 Hz, $J_{2C\text{-}F}$ = 8.6 Hz), 129.7 (d, $J_{C\text{-}P}$ = 11.9 Hz), 130.2 (d, $J_{C\text{-}P}$ = 12.6 Hz), 131.1 (d, $J_{C\text{-}P}$ = 12.3 Hz), 134.5 (d, $J_{C\text{-}P}$ = 6.5 Hz), 135.3 (d, $J_{C\text{-}P}$ = 9.9 Hz), 135.7 (d, $J_{C\text{-}P}$ = 9.4 Hz), 135.7 (overlapped), 136.0 (d, $J_{C\text{-}P}$ = 2.8 Hz), 136.3 (d, $J_{C\text{-}P}$ = 2.7 Hz), 143.5 (d, $J_{C\text{-}P}$ = 3.7 Hz), 163.0 (dd, $J_{1C\text{-}P}$ = 3.8 Hz, $J_{2C\text{-}F}$ = 247.0 Hz). ^{31}P NMR (243 MHz, DMSO-d_6) δ 2.94. HRMS (MALDI-TOF) m/z [M − Br^-] Calcd for $C_{26}H_{21}FOP^+$ 399.1309; Found 399.1309.

*2-(4-Bromophenyl)-1,1-diphenyl-2,4-dihydro-1H-benzo[d][1,3]-oxaphosphinin-1-ium Tetrafluoroborate (**3hb**).* A white solid, yield: 281.5 mg, 73%; mp: 215−217 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 5.61 (s, 2 H), 6.86 (d, 2 H, J = 7.6 Hz), 7.01 (dd, 2 H, J_1 = 8.0 Hz, $J_{2C\text{-}P}$ = 12.0 Hz), 7.35 (d, 1 H, $J_{C\text{-}P}$ = 2.8 Hz), 7.54 (d, 2 H, J = 8.0 Hz), 7.60−7.70 (m, 4 H), 7.74−7.79 (m, 1 H), 7.85−8.05 (m, 5 H), 8.21

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(dd, 2 H, J_1 = 8.0 Hz, $J_{2C\text{-}P}$ = 12.0 Hz). ^{13}C NMR (100 MHz, DMSO-d_6) δ 71.4, 74.7 (d, $J_{C\text{-}P}$ = 55.9 Hz), 113.2 (d, $J_{C\text{-}P}$ = 80.8 Hz), 114.1 (d, $J_{C\text{-}P}$ = 84.2 Hz), 116.1 (d, $J_{C\text{-}P}$ = 78.8 Hz), 123.6 (d, $J_{C\text{-}P}$ = 4.4 Hz), 127.1 (d, $J_{C\text{-}P}$ = 8.7 Hz), 128.7 (d, $J_{C\text{-}P}$ = 4.6 Hz), 129.7 (d, $J_{C\text{-}P}$ = 11.8 Hz), 130.3 (d, $J_{C\text{-}P}$ = 12.7 Hz), 130.7 (d, $J_{C\text{-}P}$ = 2.6 Hz), 131.2 (d, $J_{C\text{-}P}$ = 12.3 Hz), 132.3 (d, $J_{C\text{-}P}$ = 2.5 Hz), 134.6 (d, $J_{C\text{-}P}$ = 6.7 Hz), 135.2 (d, $J_{C\text{-}P}$ = 9.9 Hz), 135.7 (d, $J_{C\text{-}P}$ = 9.6 Hz), 135.7 (overlapped), 136.2 (d, $J_{C\text{-}P}$ = 2.3 Hz), 136.4 (d, $J_{C\text{-}P}$ = 2.9 Hz), 143.5 (d, $J_{C\text{-}P}$ = 3.7 Hz). ^{31}P NMR (162 MHz, DMSO-d_6) δ 2.92. ^{11}B-NMR (128 MHz, DMSO-d_6) δ −1.16. ^{19}F-NMR (376 MHz, DMSO-d_6) δ −148.20, −48.15. HRMS (MALDI-TOF) m/z [M − F_4B^-] Calcd for $C_{26}H_{21}BrOP^+$ 459.0508; Found 459.0515.

*2-(Naphthalen-1-yl)-1,1-diphenyl-2,4-dihydro-1H-benzo[d][1,3]-oxaphosphinin-1-ium Tetrafluoroborate (**3ib**).* A white solid, yield: 272.9 mg, 75%; mp: 228−230 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 5.63 (d, 1 H, J = 16.2 Hz), 5.79 (d, 1 H, $J_{C\text{-}P}$ = 16.2 Hz), 6.81−6.87 (m, 2 H), 6.92−6.99 (m, 1 H), 7.15 (dd, 1 H, J_1 = 7.2 Hz, J_2 =7.2 Hz), 7.36 (dd, 1 H, J_1 = 6.6 Hz, J_2 =7.8 Hz), 7.46 (dd, 1 H, J_1 = 4.0 Hz, J_2 =7.2 Hz), 7.51−7.56 (m, 2 H), 7.56−7.61 (m, 1 H), 7.63−7.75 (m, 4 H), 7.78−7.82 (m, 1 H), 7.83−7.89 (m, 2 H), 7.91 (s, 1 H), 7.95−8.04 (m, 5 H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 71.7, 75.1 (d, $J_{C\text{-}P}$ = 54.8 Hz), 113.2 (d, $J_{C\text{-}P}$ = 80.2 Hz), 114.1 (d, $J_{C\text{-}P}$ = 83.1 Hz), 116.9 (d, $J_{C\text{-}P}$ = 77.1 Hz), 123.6, 125.5 (d, $J_{C\text{-}P}$ = 3.2 Hz), 127.1 (d, $J_{C\text{-}P}$ = 8.5 Hz), 126.5, 126.7, 127.3 (d, $J_{C\text{-}P}$ = 3.0 Hz), 127.4 (d, $J_{C\text{-}P}$ = 6.1 Hz), 129.3, 129.5 (d, $J_{C\text{-}P}$ = 3.8 Hz), 129.7 (d, $J_{C\text{-}P}$ = 12.0 Hz), 130.1 (d, $J_{C\text{-}P}$ = 12.4 Hz), 130.7 (d, $J_{C\text{-}P}$ = 12.7 Hz), 130.8 (d, $J_{C\text{-}P}$ = 5.0 Hz), 133.6 (d, $J_{C\text{-}P}$ = 2.0 Hz), 135.09 (d, $J_{C\text{-}P}$ = 5.6 Hz), 135.11 (d, $J_{C\text{-}P}$ = 10.3 Hz), 135.83, 135.84 (d, $J_{C\text{-}P}$ = 9.0 Hz), 135.9, 136.1 (d, $J_{C\text{-}P}$ = 2.4 Hz), 144.2 (d, $J_{C\text{-}P}$ = 3.6 Hz). ^{31}P NMR (162 MHz, DMSO-d_6) δ 3.16. ^{11}B-NMR (128 MHz, DMSO-d_6) δ −1.14. ^{19}F-NMR (376 MHz, DMSO-d_6) δ −148.20, −148.14. HRMS (MALDI-TOF) m/z [M − F_4B^-] Calcd for $C_{30}H_{24}OP^+$ 431.1559; Found 431.1562.

*1,1-Diphenyl-2-(p-tolyl)-2,4-dihydro-1H-benzo[d][1,3]oxaphosphinin-1-ium Tetrafluoroborate (**3jb**).* A white solid, yield: 289.5 mg, 86%; mp: 214−216 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 2.26 (s, 3 H), 5.56 (d, 1 H, J = 16.5 Hz), 5.61 (d, 1 H, J = 16.5 Hz), 6.80 (d, 2 H, J = 7.0 Hz), 5.98−7.03 (m, 2 H), 7.10 (d, 2 H, J = 7.0 Hz), 7.27 (s, 1 H), 7.58−7.65 (m, 4 H),7.72−7.77 (m, 1 H), 7.82−7.87 (m, 2 H), 7.87−7.91 (m, 1 H), 7.91−7.95 (m, 1 H), 7.96−8.00 (m, 1 H), 8.14−8.19 (m, 2 H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 20.7, 70.9, 74.7 (d, $J_{C\text{-}P}$ = 56.1 Hz), 112.9 (d, $J_{C\text{-}P}$ = 80.5 Hz), 113.8 (d, $J_{C\text{-}P}$ = 85.0 Hz), 116.0 (d, $J_{C\text{-}P}$ = 79.4 Hz), 126.2, 126.5 (d, $J_{C\text{-}P}$ = 4.8 Hz), 127.7 (d, $J_{C\text{-}P}$ = 2.3 Hz), 129.1 (d, $J_{C\text{-}P}$ = 11.4 Hz), 129.3, 129.6 (d, $J_{C\text{-}P}$ = 12.5 Hz), 130.6 (d, $J_{C\text{-}P}$ = 12.0 Hz), 134.1, 134.6 (d, $J_{C\text{-}P}$ = 9.4 Hz), 135.18, 135.21 (d, $J_{C\text{-}P}$ = 8.8 Hz), 135.5, 135.7, 139.4 (d, $J_{C\text{-}P}$ = 3.4 Hz), 143.0 (d, $J_{C\text{-}P}$ = 3.8 Hz). ^{31}P NMR (243 MHz, DMSO-d_6) δ 2.32. ^{11}B-NMR (128 MHz, DMSO-d_6) δ 1.13. ^{19}F-NMR (376 MHz, DMSO-d_6) δ −148.22, −148.16. HRMS (MALDI-TOF) m/z [M − F_4B^-] Calcd for $C_{27}H_{24}OP^+$ 395.1559; Found 395.1560.

*2-(4-Methoxyphenyl)-1,1-diphenyl-2,4-dihydro-1H-benzo[d][1,3]-oxaphosphinin-1-ium Tetrafluoroborate (**3kb**).* A white solid, yield: 281.0 mg, 81%; mp: 224−225 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 3.76 (s, 3 H), 5.56 (d, 1 H, J = 16.4 Hz), 5.60 (d, 1 H, J = 16.4 Hz), 6.84 (dd, 2 H, $J_{1C\text{-}P}$ = 2.0 Hz, J_2 = 8.8 Hz), 6.89 (d, 2 H, J = 8.8 Hz), 7.03 (dd, 2 H, J_1 = 7.8 Hz, $J_{2C\text{-}P}$ = 12.2 Hz), 7.24 (d, 1 H, J = 5.6 Hz), 7.59−7.70 (m, 4 H), 7.75 (dd, 1 H, $J_{1C\text{-}P}$ = 6.4 Hz, $J_{2C\text{-}P}$ = 7.2 Hz), 7.83−7.89 (m, 2 H), 7.90−7.83 (m, 3 H), 8.17 (dd, 2 H, J_1 = 7.8 Hz, $J_{2C\text{-}P}$ = 12.2 Hz). ^{13}C NMR (100 MHz, DMSO-d_6) δ 55.8, 71.5, 75.1 (d, $J_{C\text{-}P}$ = 56.4 Hz), 113.5 (d, $J_{C\text{-}P}$ = 79.0 Hz), 114.4 (d, $J_{C\text{-}P}$ = 84.5 Hz), 114.7 (d, $J_{C\text{-}P}$ = 1.9 Hz), 116.6 (d, $J_{C\text{-}P}$ = 78.8 Hz), 122.9 (d, $J_{C\text{-}P}$ = 2.5 Hz), 127.1 (d, $J_{C\text{-}P}$ = 8.7 Hz), 128.3 (d, $J_{C\text{-}P}$ = 4.6 Hz), 129.7 (d, $J_{C\text{-}P}$ = 11.8 Hz), 130.2 (d, $J_{C\text{-}P}$ = 12.5 Hz), 131.1 (d, $J_{C\text{-}P}$ = 12.2 Hz), 134.6 (d, $J_{C\text{-}P}$ = 6.0 Hz), 135.1 (d, $J_{C\text{-}P}$ = 9.6 Hz), 135.7, 135.8 (d, $J_{C\text{-}P}$ = 9.4 Hz), 136.0 (d, $J_{C\text{-}P}$ = 2.2 Hz), 136.3 (d, $J_{C\text{-}P}$ = 1.9 Hz), 143.6 (d, $J_{C\text{-}P}$ = 3.7 Hz), 160.7 (d, $J_{C\text{-}P}$ = 3.1 Hz). ^{31}P NMR (162 MHz, DMSO-d_6) δ 1.86. ^{11}B-NMR (128 MHz, DMSO-d_6) δ 1.26. ^{19}F-NMR (376 MHz, DMSO-d_6) δ −148.31, −148.25. HRMS (MALDI-TOF) m/z [M − F_4B^-] Calcd for $C_{27}H_{24}O_2P^+$ 411.1508; Found 411.1511.

*2-(3,4-Dimethoxyphenyl)-1,1-diphenyl-2,4-dihydro-1H-benzo[d]-[1,3]oxaphosphinin-1-ium Tetrafluoroborate (**3 lb**).* A white solid, yield: 330.2 mg, 89%; mp: 209−210 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 3.28 (s, 3 H), 3.72 (s, 3 H), 5.53 (d, 1 H, J = 16.4 Hz), 5.57 (d, 1 H, J = 16.4 Hz), 6.13 (s, 1 H), 6.62 (d, 1 H, J = 8.2 Hz), 6.91 (d, 1 H, J = 8.2 Hz), 7.01(dd, 2 H, J_1 = 7.4 Hz, $J_{2C\text{-}P}$ = 12.2 Hz), 7.20 (d, 1 H, J = 5.6 Hz), 7.59−7.67 (m, 4 H), 7.69−7.76 (m, 1 H), 7.82 (ddd, 2 H, $J_{1C\text{-}P}$ = 3.3 Hz, J_2 = 7.6 Hz, J_3 = 7.8 Hz), 7.87−7.89 (m, 3 H), 8.16 (dd, 2 H, J_1 = 7.6 Hz, $J_{2C\text{-}P}$ = 12.4 Hz). ^{13}C NMR (151 MHz, DMSO-d_6) δ 54.8, 55.5 (d, $J_{C\text{-}P}$ = 9.7 Hz), 70.1, 74.7 (d, $J_{C\text{-}P}$ = 56.8 Hz), 109.2, 111.5, 113.0 (d, $J_{C\text{-}P}$ = 79.3 Hz), 114.2 (d, $J_{C\text{-}P}$ = 85.0 Hz), 116.0 (d, $J_{C\text{-}P}$ = 80.0 Hz), 119.2, 122.4, 126.5 (d, $J_{C\text{-}P}$ = 10.0 Hz), 129.1 (d, $J_{C\text{-}P}$ = 11.3 Hz), 129.7 (d, $J_{C\text{-}P}$ = 12.5 Hz), 130.5 (d, $J_{C\text{-}P}$ = 11.0 Hz), 134.1 (d, $J_{C\text{-}P}$ = 5.0 Hz), 134.7 (d, $J_{C\text{-}P}$ = 10.0 Hz), 135.2, 135.37 (d, $J_{C\text{-}P}$ = 8.8 Hz), 135.39, 135.7, 143.1 (d, $J_{C\text{-}P}$ = 3.6 Hz), 148.5 (d, $J_{C\text{-}P}$ = 1.8 Hz), 149.7 (d, $J_{C\text{-}P}$ = 3.5 Hz). ^{31}P NMR (162 MHz, DMSO-d_6) δ 1.63. ^{11}B-NMR (128 MHz, DMSO-d_6) δ −1.17. ^{19}F-NMR (376 MHz, DMSO-d_6) δ −148.24, −148.19. HRMS (MALDI-TOF) m/z [M − F_4B^-] Calcd for $C_{28}H_{26}O_3P^+$ 441.1614; Found 441.1613.

*2-(2,4-Dimethoxyphenyl)-1,1-diphenyl-2,4-dihydro-1H-benzo[d]-[1,3]oxaphosphinin-1-ium Tetrafluoroborate (**3mb**).* A white solid, yield: 238.8 mg, 84%; mp: 115−117 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 3.35 (s, 3 H), 3.74 (s, 3 H), 5.48 (d, 1 H, J = 16.2 Hz), 5.68 (d, 1 H, J = 16.2 Hz), 6.36 (d, 1 H, J = 7.6 Hz), 6.53 (dd, 1 H, $J_{1C\text{-}P}$ = 2.2 Hz, J_2 = 8.6 Hz), 6.56 (s, 1 H), 7.06 (dd, 2 H, J_1 = 8.0 Hz, $J_{2C\text{-}P}$ = 11.6 Hz), 7.21 (d, 1 H, J = 5.6 Hz), 7.52 (dd, 1 H, J_1 = 7.8 Hz, $J_{2C\text{-}P}$ = 13.0 Hz), 7.56−7.65 (m, 3 H), 7.68−7.74 (m, 1 H), 7.75−7.82 (m, 2 H), 7.83−7.95 (m, 3 H), 8.06 (dd, 2 H, J_1 = 7.8 Hz, $J_{2C\text{-}P}$ = 12.6 Hz). ^{13}C NMR (100 MHz, DMSO-d_6) δ 55.1, 55.9, 71.2, 72.6 (d, $J_{C\text{-}P}$ = 55.1 Hz), 98.4 (d, $J_{C\text{-}P}$ = 1.3 Hz), 106.1, 111.7 (d, $J_{C\text{-}P}$ = 2.5 Hz), 114.2 (d, $J_{C\text{-}P}$ = 78.6 Hz), 114.5 (d, $J_{C\text{-}P}$ = 83.3 Hz), 118.1 (d, $J_{C\text{-}P}$ = 78.4 Hz), 127.0 (d, $J_{C\text{-}P}$ = 8.6 Hz), 129.0 (d, $J_{C\text{-}P}$ =4.1 Hz), 129.5 (d, $J_{C\text{-}P}$ = 11.6 Hz), 130.0 (d, $J_{C\text{-}P}$ = 12.3 Hz), 130.2 (d, $J_{C\text{-}P}$ = 12.5 Hz), 134.8 (d, $J_{C\text{-}P}$ = 6.9 Hz), 134.9 (d, $J_{C\text{-}P}$ = 13.0 Hz), 135.42, 135.45, 135.50 (d, $J_{C\text{-}P}$ = 9.4 Hz), 135.7 (d, $J_{C\text{-}P}$ = 2.5 Hz), 144.0 (d, $J_{C\text{-}P}$ = 3.7 Hz), 156.6 (d, $J_{C\text{-}P}$ = 4.2 Hz), 162.0 (d, $J_{C\text{-}P}$ = 3.0 Hz). ^{31}P NMR (162 MHz, DMSO-d_6) δ 1.39. ^{11}B-NMR (128 MHz, DMSO-d_6) δ −1.26. ^{19}F-NMR (376 MHz, DMSO-d_6) δ −148.30, −148.24. HRMS (MALDI-TOF) m/z [M − F_4B^-] Calcd for $C_{28}H_{26}O_3P^+$ 441.1614; Found 441.1617.

*1,1-Diphenyl-2-(3,4,5-trimethoxyphenyl)-2,4-dihydro-1H-benzo-[d][1,3]oxaphosphinin-1-ium Tetrafluoroborate (**3nb**).* A white solid, yield: 320.4 mg, 82%; mp: 213-214 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 3.38 (s, 6 H), 3.64 (s, 3 H), 5.57 (s, 2 H), 6.08 (d, 2 H, $J_{C\text{-}P}$ = 2.0 Hz), 6.98(dd, 2 H, J_1 = 7.8 Hz, $J_{2C\text{-}P}$ = 12.2 Hz), 7.17 (d, 1 H, J = 4.8 Hz), 7.60−7.67 (m, 4 H), 7.68−7.75 (m, 1 H), 7.81−8.01 (m, 5 H), 8.20 (dd, 2 H, J_1 = 7.6 Hz, $J_{2C\text{-}P}$ = 12.4 Hz). ^{13}C NMR (151 MHz, DMSO-d_6) δ 55.5, 60.3, 70.8 (d, $J_{C\text{-}P}$ = 1.5 Hz), 75.0 (d, $J_{C\text{-}P}$ = 56.2 Hz), 103.4, 112.6 (d, $J_{C\text{-}P}$ = 79.9 Hz), 114.1 (d, $J_{C\text{-}P}$ = 84.9 Hz), 115.9 (d, $J_{C\text{-}P}$ = 80.3 Hz), 125.9 (d, $J_{C\text{-}P}$ = 2.7 Hz), 126.6 (d, $J_{C\text{-}P}$ = 9.4 Hz), 129.2 (d, $J_{C\text{-}P}$ = 11.2 Hz), 129.6 (d, $J_{C\text{-}P}$ = 12.4 Hz), 130.5 (d, $J_{C\text{-}P}$ = 12.2 Hz), 134.2 (d, $J_{C\text{-}P}$ = 6.3 Hz), 134.8 (d, $J_{C\text{-}P}$ = 9.8 Hz), 135.2 (overlapped), 135.3 (d, $J_{C\text{-}P}$ = 8.8 Hz), 135.6, 135.7, 138.2 (d, $J_{C\text{-}P}$ = 3.9 Hz), 143.0 (d, $J_{C\text{-}P}$ = 3.2 Hz), 152.9 (d, $J_{C\text{-}P}$ = 3.2 Hz). ^{31}P NMR (162 MHz, DMSO-d_6) δ 2.51. ^{11}B-NMR (128 MHz, DMSO-d_6) δ −1.28. ^{19}F-NMR (376 MHz, DMSO-d_6) δ −148.27, −148.21. HRMS (MALDI-TOF) m/z [M − F_4B^-] Calcd for $C_{29}H_{28}O_4P^+$ 471.1720; Found 471.1725.

*(E)-1,1-Diphenyl-2-styryl-2,4-dihydro-1H-benzo[d][1,3]oxaphosphinin-1-ium Tetrafluoroborate (**3ob**).* A white solid, yield: 300.2 mg, 87%; mp: 105−106 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 5.46 (s, 2 H), 6.36 (ddd, 1 H, J_1 = 4.5 Hz, J_2 = 5.7 Hz, J_3 = 15.9 Hz), 6.65 (dd, 1 H, J_1 = 4.5 Hz, J_2 = 15.9 Hz), 6.82 (d, 1 H, J = 4.5 Hz), 7.29−7.34 (m, 3 H), 7.36−7.42 (m, 2 H), 7.57 (dd, 2 H, $J_{1C\text{-}P}$ = 8.1 Hz, J_2 = 12.2 Hz), 7.61−7.66 (m, 1 H), 7.66−7.76 (m, 4 H), 7.81−7.86 (m, 2 H), 7.87−7.93 (m, 2 H), 7.95−8.00 (m, 1 H), 8.11 (dd, 2 H, J_1 = 7.8 Hz, $J_{2C\text{-}P}$ = 11.4 Hz). ^{13}C NMR (100 MHz, DMSO-d_6) δ 70.5 (d, $J_{C\text{-}P}$ = 2.5 Hz), 74.4 (d, $J_{C\text{-}P}$ = 57.8 Hz), 113.2 (d, $J_{C\text{-}P}$ = 79.7 Hz), 115.7 (d, $J_{C\text{-}P}$ = 81.7 Hz), 116.6 (d, $J_{C\text{-}P}$ = 77.2 Hz), 118.3 (d, $J_{C\text{-}P}$ = 4.1 Hz), 127.1 (d, $J_{C\text{-}P}$ = 8.7 Hz), 127.4 (d, $J_{C\text{-}P}$ = 1.1 Hz), 129.2, 129.4, 129.6 (d, $J_{C\text{-}P}$ = 11.8 Hz), 130.4 (d, $J_{C\text{-}P}$ = 12.6 Hz), 131.0 (d, $J_{C\text{-}P}$ = 12.2 Hz), 134.4 (d, $J_{C\text{-}P}$ = 6.2 Hz), 134.9 (d, $J_{C\text{-}P}$ = 9.6 Hz), 135.3 (d, $J_{C\text{-}P}$ = 3.4 Hz), 135.6, 135.7(d, $J_{C\text{-}P}$ = 9.9 Hz), 135.9 (d, $J_{C\text{-}P}$ = 2.8 Hz), 136.1 (d, $J_{C\text{-}P}$ = 2.6

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Hz), 136.7 (d, $J_{C\text{-}P}$ = 12.1 Hz), 143.5 (d, $J_{C\text{-}P}$ = 3.9 Hz). ^{31}P NMR (162 MHz, DMSO-d_6) δ −0.41. ^{11}B-NMR (128 MHz, DMSO-d_6) δ −1.28. ^{19}F-NMR (376 MHz, DMSO-d_6) δ −148.27, −148.22. HRMS (MALDI-TOF) m/z [M − F_4B^-] Calcd for $C_{28}H_{24}OP^+$ 407.1559; Found 407.1558.

*2-Isopropyl-1,1-diphenyl-2,4-dihydro-1H-benzo[d][1,3]oxaphosphinin-1-ium Bromide (**3pa**).* A white solid, yield: 187.1 mg, 63%; mp: 215−216 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 0.87 (d, 3 H, J = 6.8 Hz), 1.01 (d, 3 H, J = 6.4 Hz), 1.78−1.91 (m, 1 H), 5.33 (d, 1 H, J = 17.6 Hz, 1 H), 5.37 (d, 1 H, J = 17.6 Hz), 5.76 (dd, 1 H, J_1 = 8.8 Hz, $J_{2C\text{-}P}$ = 8.8 Hz), 7.46 (dd, 1 H, J_1 = 8.0 Hz, $J_{2C\text{-}P}$ = 13.6 Hz), 7.55 (ddd, 1 H, $J_{1C\text{-}P}$ = 1.7 Hz, J_2 = 7.2 Hz, J_3 = 7.4 Hz), 7.60−7.71 (m, 3 H), 7.76−7.87 (m, 5 H), 7.90−8.00 (m, 2 H), 8.13 (d, 2 H, J = 7.8 Hz, $J_{2C\text{-}P}$ = 12.2 Hz). ^{13}C NMR (151 MHz, DMSO-d_6) δ 18.3 (dd, $J_{1C\text{-}P}$ = 2.2 Hz, $J_{2C\text{-}P}$ = 11.4 Hz), 19.2 (d, $J_{C\text{-}P}$ = 1.2 Hz), 30.1 (d, $J_{C\text{-}P}$ = 5.6 Hz), 70.6 (ddd, $J_{1C\text{-}P}$ = 2.3 Hz, $J_{2C\text{-}P}$ = 9.5 Hz, $J_{3C\text{-}P}$ = 10.4 Hz), 78.0 (dd, $J_{1C\text{-}P}$ = 6.4 Hz, $J_{2C\text{-}P}$ = 55.2 Hz), 113.9 (d, $J_{C\text{-}P}$ = 84. Hz), 114.6 (d, $J_{C\text{-}P}$ = 82.3 Hz), 118.1 (d, $J_{C\text{-}P}$ = 76.0 Hz), 126.2 (d, $J_{C\text{-}P}$ = 4.8 Hz), 129.0 (d, $J_{C\text{-}P}$ = 11.0 Hz), 130.4 (d, $J_{C\text{-}P}$ = 11.6 Hz), 133.6 (d, $J_{C\text{-}P}$ = 5.6 Hz), 134.2 (d, $J_{C\text{-}P}$ = 9.8 Hz), 134.7 (d, $J_{C\text{-}P}$ = 2.1 Hz), 135.1 (d, $J_{C\text{-}P}$ = 10.1 Hz), 135.4 (d, $J_{C\text{-}P}$ = 2.0 Hz), 143.0 (d, $J_{C\text{-}P}$ = 2.1 Hz). ^{31}P NMR (162 MHz, DMSO-d_6) δ 1.81. HRMS (MALDI-TOF) m/z [M − Br^-] Calcd for $C_{23}H_{24}OP^+$ 347.1559; Found 347.1560.

*2-(Furan-2-yl)-1,1-diphenyl-2,4-dihydro-1H-benzo[d][1,3]-oxaphosphinin-1-ium Bromide (**3qa**).* A white solid, yield: 202.3 mg, 64%, mp: 223−224 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 5.45 (dd, 1 H, $J_{1C\text{-}P}$ = 2.0 Hz, J_2 = 16.4 Hz), 5.55 (d, 1 H, $J_{C\text{-}P}$ = 16.4 Hz), 6.40 (dd, 1 H, J_1 = 3.2 Hz, J_2 = 3.2 Hz), 6.50 (s, 1 H), 7.25 (dd, 2 H, J_1 = 7.8 Hz, $J_{2C\text{-}P}$ = 13.0 Hz), 7.49 (s, 1 H), 7.61−7.72 (m, 5 H), 7.73−7.78 (m, 1 H), 7.79−7.85 (m, 2 H), 7.88−8.00 (m, 3 H), 8.11 (dd, 2 H, J_1 = 7.8 Hz, $J_{2C\text{-}P}$ = 12.6 Hz). ^{13}C NMR (151 MHz, DMSO-d_6) δ 69.6 (d, $J_{C\text{-}P}$ = 60.6 Hz), 70.2 (d, $J_{C\text{-}P}$ = 2.4 Hz), 111.3, 112.1 (overlapped), 112.4 (d, $J_{C\text{-}P}$ = 80.8 Hz), 115.4 (d, $J_{C\text{-}P}$ = 83.7 Hz), 116.1 (d, $J_{C\text{-}P}$ = 84.0 Hz), 126.7 (d, $J_{C\text{-}P}$ = 8.3 Hz), 129.1 (d, $J_{C\text{-}P}$ = 12.1 Hz), 129.9 (d, $J_{C\text{-}P}$ = 12.5 Hz), 130.4 (d, $J_{C\text{-}P}$ = 12.2 Hz), 133.9 (d, $J_{C\text{-}P}$ = 6.5 Hz), 134.6 (d, $J_{C\text{-}P}$ = 13.0 Hz), 134.7 (d, $J_{C\text{-}P}$ = 10.7 Hz), 135.2, 135.5, 135.7, 142.9 (d, $J_{C\text{-}P}$ = 3.3 Hz), 143.7 (d, $J_{C\text{-}P}$ = 4.1 Hz), 145.0. ^{31}P NMR (243 MHz, DMSO-d_6) δ −0.71. HRMS (MALDI-TOF) m/z [M − Br^-] Calcd for $C_{24}H_{20}O_2P^+$ 371.1195; Found 371.1196.

General Procedure for the Wittig Olefination Using Phosphonium Salts 3 and K_2CO_3 as a Base. To a testing tube (10 mL) were added phosphonium salt **3** (0.35 mmol), aldehyde **2** (0.31 mmol), K_2CO_3 (58.0 mg, 0.42 mmol), DMSO (1.0 mL), and CH_3CN (0.2 mL). After it was stirred at rt overnight, the reaction mixture was diluted with water (10 mL), and extracted with CH_2Cl_2 (10 mL × 2). The combined extract was evaporated, and the residue was isolated by preparative TLC (silica gel) to afford vinyl ethers **4**.

General Procedure for the Wittig Olefination Using Phosphonium Salts 3 and *t*-BuOK as a Base. To a mixture of phosphonium salt **3** (0.3 mmol), aldehyde **2** (0.3 mmol), and anhyd THF (5 mL) in a round-bottom flask (25 mL) was added *t*-BuOK (1 M in THF, 0.36 mL) dropwise, and the reaction mixture immediately turned to dark-red. After it was stirred at rt for 3 h, the mixture was diluted with CH_2Cl_2 (10 mL), evaporated, and isolated by preparative TLC (silica gel) to give vinyl ethers **4**.

*(2-(((2-(4-Chlorophenyl)-1-phenylvinyl)oxy)methyl)phenyl)-diphenylphosphine Oxide (**4ab**).* A white solid isolated as an inseparable Z/E mixture (Z:E = 89:11 based on integrations of two peaks at 5.06 and 5.34 of ^{1}H NMR), yield: 160.4 mg, 61%; R_f: 0.50 (PE:EtOAc = 1:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ: Z-isomer, 5.06 (s, 2 H), 6.37 (s, 1 H), 7.08 (dd, 1 H, J_1 = 7.6 Hz, $J_{2C\text{-}P}$ = 13.8 Hz), 7.14−7.18 (m, 1 H), 7.29 (d, 2 H, J = 6.4 Hz), 7.35−7.39 (m, 2 H), 7.41−7.46 (m, 2 H), 7.48−7.55 (m, 8 H), 7.57−7.63 (m, 4 H), 7.64−7.72 (m, 1 H), 7.73−7.79 (m, 1 H), 8.04 (d, 1 H, $J_{1C\text{-}P}$ = 3.4 Hz, J_2 = 7.4 Hz); E-isomer (part), 5.34 (s, 2 H), 5.69 (s, 1 H), 6.80 (d, 2 H, J = 8.4 Hz). ^{13}C NMR (100 MHz, DMSO-d_6) δ: Z-isomer, 69.6 (d, $J_{C\text{-}P}$ = 7.1 Hz), 112.4, 126.4, 127.8 (d, $J_{C\text{-}P}$ = 12.1 Hz), 128.1 (d, $J_{C\text{-}P}$ = 9.7 Hz), 128.8, 129.1, 129.2, 129.3 (d, $J_{C\text{-}P}$ = 11.8 Hz), 129.9 (d, $J_{C\text{-}P}$ = 90.8 Hz), 130.4, 131.4, 131.8 (d, $J_{C\text{-}P}$ = 9.7 Hz), 132.58, 132.62 (d, $J_{C\text{-}P}$ = 107.2 Hz), 133.0, 133.1 (d, $J_{C\text{-}P}$ = 6.5 Hz), 134.6, 135.6, 142.3 (d, $J_{C\text{-}P}$ = 7.1 Hz), 155.2. ^{31}P NMR (162 MHz, DMSO-d_6) δ 28.94 (E-isomer), 29.17 (Z-isomer). HRMS (MALDI-TOF) m/z [M + Na]$^+$ Calcd for $C_{33}H_{26}ClNaO_2P^+$ 543.1251; Found 543.1255.

*(2-(((2-(4-Nitrophenyl)-1-phenylvinyl)oxy)methyl)phenyl)-diphenylphosphine Oxide (**4ad**).* A yellow solid isolated as an inseparable Z/E mixture (Z:E = 85:15 based on integrations of two peaks at 6.37 and 5.82 of ^{1}H NMR), yield: 179.6 mg, 84%; R_f: 0.53 (PE:EtOAc 1:1). ^{1}H NMR (600 MHz, DMSO-d_6) δ: Z-isomer, 5.07 (s, 2 H), 6.37 (s, 1 H), 7.04 (dd, 1 H, J_1 = 7.8 Hz, $J_{2C\text{-}P}$ = 13.3 Hz), 7.35−7.42 (m, 3 H), 7.43−7.59 (m, 12 H), 7.60−7.68 (m, 1 H), 7.71−7.75 (m, 1 H), 7.76 (d, 2 H, J = 8.3 Hz), 7.95 (d, 1 H, $J_{C\text{-}P}$ = 5.8 Hz), 8.04 (d, 2 H, J = 8.3 Hz) ; E-isomer (part), 5.36 (s, 2 H), 5.82 (s, 1 H), 6.95 (d, 2 H, J = 8.2 Hz), 7.09−7.16 (m, 3 H), 7.29 (dd, 1 H, $J_{1C\text{-}P}$ = 7.3 Hz, J_2 = 7.3 Hz), 7.92 (d, 2 H, J = 8.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: Z-isomer, 70.1 (d, $J_{C\text{-}P}$ = 4.8 Hz), 111.0, 123.6, 126.9, 127.1 (d, $J_{C\text{-}P}$ = 12.6 Hz), 128.0 (d, $J_{C\text{-}P}$ = 9.7 Hz), 128.5, 128.6, 128.7 (d, $J_{C\text{-}P}$ = 10.8 Hz), 129.3, 129.6 (d, $J_{C\text{-}P}$ = 100.4 Hz), 131.8 (d, $J_{C\text{-}P}$ = 9.8 Hz), 132.0, 132.1 (d, $J_{C\text{-}P}$ = 102.9 Hz), 132.4, 133.3 (d, $J_{C\text{-}P}$ = 12.2 Hz), 135.2, 142.4 (d, $J_{C\text{-}P}$ = 7.2 Hz), 142.8, 145.3, 159.1; E-isomer (part), 60.4, 101.8, 123.2, 144.7, 144.9, 159.2. ^{31}P NMR (243 MHz, $CDCl_3$) δ 31.44 (Z-isomer), 31.61 (E-isomer). HRMS (QFT-ESI) m/z [M + Na]$^+$ Calcd for $C_{33}H_{26}NNaO_4P^+$ 554.1492; Found 554.1495.

*(2-(((2-(2-Nitrophenyl)-1-phenylvinyl)oxy)methyl)phenyl)-diphenylphosphine Oxide (**4ae**).* A yellow solid isolated as an inseparable Z/E mixture (Z:E = 40:60 based on integrations of two peaks at 5.03 and 5.43 of ^{1}H NMR), yield: 158.7 mg, 75%; R_f: 0.53 (PE:EtOAc 1:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ: E-isomer, 5.43 (s, 2 H), 5.81 (s, 1 H), 7.02 (dd, 1 H, J_1 = 7.5 Hz, $J_{2C\text{-}P}$ = 13.1 Hz), 7.10−7.18 (m, 4 H), 7.19−7.32 (m, 3 H), 7.33−7.40 (m, 3 H), 7.42−7.62 (m, 8 H), 7.67−7.73 (m, 3 H), 7.74−7.81 (m, 1 H), 7.85−7.90 (m, 1 H); Z-isomer (part), 5.03 (s, 2 H), 6.42 (s, 1 H), 6.77 (d, 2 H, J = 6.8 Hz). ^{13}C NMR (151 MHz, $CDCl_3$) δ: E-isomer, 68.4 (d, $J_{C\text{-}P}$ = 4.6 Hz), 99.7, 124.3, 126.9, 127.0 (d, $J_{C\text{-}P}$ = 12.8 Hz), 128.0, 128.4 (d, $J_{C\text{-}P}$ = 10.1 Hz), 128.5, 128.7 (d, $J_{C\text{-}P}$ = 12.1 Hz), 129.4 (d, $J_{C\text{-}P}$ = 100.9 Hz), 129.5, 130.4, 131.9, 131.9 (overlapped), 132.1 (d, $J_{C\text{-}P}$ = 8.9 Hz), 132.5, 132.7 (d, $J_{C\text{-}P}$ = 100.7 Hz), 133.2 (d, $J_{C\text{-}P}$ = 12.1 Hz), 133.5, 135.0, 141.9 (d, $J_{C\text{-}P}$ = 7.2 Hz), 148.3, 157.4; Z-isomer (part): 70.4 (d, $J_{C\text{-}P}$ = 4.6 Hz), 106.9, 126.4, 126.82, 126.84 (d, $J_{C\text{-}P}$ = 11.9 Hz), 128.1 (d, $J_{C\text{-}P}$ = 11.0 Hz), 128.6 (d, $J_{C\text{-}P}$ = 12.3 Hz), 128.8, 129.0, 129.6 (d, $J_{C\text{-}P}$ = 100.5 Hz), 129.7, 131.7, 131.8 (d, $J_{C\text{-}P}$ = 9.8 Hz), 132.2 (d, $J_{C\text{-}P}$ = 103.3 Hz), 132.25, 133.1 (d, $J_{C\text{-}P}$ = 12.2 Hz), 132.34, 135.3, 142.4 (d, $J_{C\text{-}P}$ = 7.0 Hz), 148.0, 157.5. ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.05 (E-isomer), 31.09 (Z-isomer). HRMS (QFT-ESI) m/z [M + Na]$^+$ Calcd for $C_{33}H_{26}NNaO_4P^+$ 554.1492; Found 554.1493.

*(2-(((2-(4-Bromophenyl)-1-phenylvinyl)oxy)methyl)phenyl)-diphenylphosphine Oxide (**4ah**).* A white solid isolated as an inseparable Z/E mixture (Z:E = 89:11 based on integrations of two peaks at 4.99 and 5.28 of ^{1}H NMR), yield: 158.6 mg, 70%; R_f: 0.58 (PE:EtOAc 1:1). ^{1}H NMR (600 MHz, DMSO-d_6) δ: Z-isomer, 4.99 (s, 2 H), 6.32 (s, 1 H), 7.03 (dd, 1 H, J_1 = 7.5 Hz, $J_{2C\text{-}P}$ = 13.5 Hz), 7.31−7.36 (m, 3 H), 7.39 (d, 2 H, J = 7.8 Hz), 7.44−7.52 (m, 12 H), 7.54−7.59 (m, 2 H), 7.61−7.68 (m, 1 H), 7.71−7.75 (m, 1 H), 7.99 (d, 1 H, $J_{C\text{-}P}$ = 3.6 Hz); E-isomer (part), 5.28 (s, 2 H), 5.61 (s, 1 H), 6.70 (d, 2 H, J = 7.8 Hz), 7.09−7.13 (m, 3 H), 7.24−7.28 (m, 4 H). ^{13}C NMR (151 MHz, DMSO-d_6) δ: Z-isomer, 69.0 (d, $J_{C\text{-}P}$ = 5.1 Hz), 112.0 (d, $J_{C\text{-}P}$ = 4.2 Hz), 119.5, 125.8, 127.3 (d, $J_{C\text{-}P}$ = 12.9 Hz), 127.5 (d, $J_{C\text{-}P}$ = 9.6 Hz), 128.6, 128.7, 128.8 (d, $J_{C\text{-}P}$ = 11.8 Hz), 129.3 (d, $J_{C\text{-}P}$ = 91.9 Hz), 130.2, 131.2, 131.3 (d, $J_{C\text{-}P}$ = 9.7 Hz), 132.0 (d, $J_{C\text{-}P}$ = 102.4 Hz), 132.1, 132.56 (d, $J_{C\text{-}P}$ = 9.2 Hz), 132.59, 134.4, 135.0, 141.7 (d, $J_{C\text{-}P}$ = 7.4 Hz), 154.8. ^{31}P NMR (243 MHz, DMSO-d_6) δ 28.90 (E-isomer), 29.17 (Z-isomer). HRMS (QFT-ESI) m/z [M + Na]$^+$ Calcd for $C_{33}H_{26}BrNaO_2P^+$ 587.0746; Found 587.0752.

*(2-((((3E)-1,4-Diphenylbuta-1,3-dien-1-yl)oxy)methyl)phenyl)-diphenylphosphine Oxide (**4ao**).* A white solid isolated as an inseparable Z/E mixture (Z:E = 93:7 based on integrations of two peaks at 5.07 and 5.30 of ^{1}H NMR), yield: 91.4 mg, 45%; R_f: 0.51 (PE:EtOAc 1:1). ^{1}H NMR (600 MHz, DMSO-d_6) δ: Z-isomer, 5.07 (s, 2 H), 6.42 (d, 1 H, J = 10.4 Hz), 6.67 (d, 1 H, J = 15.6 Hz), 7.03−7.09 (m, 1 H), 7.10−7.19 (m, 1 H), 7.20−7.27 (m, 1 H), 7.27−7.35 (m, 5 H), 7.36−7.40 (m, 2 H), 7.41−7.46 (m, 3 H), 7.45−7.67 (m, 10

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H), 7.75−7.80 (m, 1 H), 8.01−8.05 (m, 1 H); *E*-isomer (part): 5.30 (s, 2 H), 5.58 (d, 1 H, J = 10.2 Hz), 6.36 (d, 1 H, J = 16.4 Hz). ^{13}C NMR (151 MHz, DMSO-d_6) δ: *Z*-isomer, 70.8 (d, $J_{C\text{-}P}$ = 4.3 Hz), 115.0, 123.2, 125.1, 126.2, 127.38 (d, $J_{C\text{-}P}$ = 10.3 Hz), 127.41, 128.4, 128.5 (d, $J_{C\text{-}P}$ = 9.4 Hz), 128.7, 128.8 (d, $J_{C\text{-}P}$ = 11.9 Hz), 129.6 (d, $J_{C\text{-}P}$ = 99.4 Hz), 131.3 (d, $J_{C\text{-}P}$ = 9.5 Hz), 131.5, 132.1, 132.3 (d, $J_{C\text{-}P}$ = 102.5 Hz), 132.5, 132.6 (d, $J_{C\text{-}P}$ = 10.8 Hz), 132.7, 134.5, 137.3, 142.0 (d, $J_{C\text{-}P}$ = 7.1 Hz), 154.0. ^{31}P NMR (243 MHz, DMSO-d_6) δ 29.08 (*E*-isomer), 29.31 (*Z*-isomer). HRMS (QFT-ESI) m/z [M + Na]$^+$ Calcd for $C_{35}H_{29}NaO_2P^+$ 535.1797; Found 535.1800.

*(2-(((2-(Furan-2-yl)-1-phenylvinyl)oxy)methyl)phenyl)diphenylphosphine Oxide (**4aq**).* A pale yellow solid isolated as an inseparable *Z*/*E* mixture (*Z*:*E* = 94:6 based on integrations of two peaks at 5.04 and 5.28 of ^{1}H NMR), yield: 152.6 mg, 80%; R_f: 0.47 (PE:EtOAc 1:1). ^{1}H NMR (600 MHz, DMSO-d_6) δ: *Z*-isomer, 5.04 (s, 2 H), 6.40−6.45 (m, 3 H), 7.04 (dd, 1 H, J_1 = 7.8 Hz, $J_{2C\text{-}P}$ = 12.8 Hz), 7.29−7.34 (m, 3 H), 7.40−7.46 (m, 2 H), 7.46−7.52 (m, 8 H),7.55−7.67 (m, 4 H), 7.72−7.79 (m, 1 H), 8.09 (d, 1 H, $J_{C\text{-}P}$ = 3.1 Hz); *E*-isomer (part): 5.28 (s, 2 H), 5.52 (s, 1 H), 5.57 (s, 1 H), 6.25 (s. One H), 7.11 (dd, 1 H, $J_{C\text{-}P}$ = 8.1 Hz, $J_{2C\text{-}P}$ = 12.8), 7.20 (d, 2 H, J = 6.7 Hz). ^{13}C NMR (151 MHz, DMSO-d_6) δ: *Z*-isomer, 68.8, 103.3 (d, $J_{C\text{-}P}$ = 10.0 Hz), 108.9 (d, $J_{C\text{-}P}$ = 12.3 Hz), 112.0 (d, $J_{C\text{-}P}$ = 12.4 Hz), 125.4, 127.2 (d, $J_{C\text{-}P}$ = 12.1 Hz), 127.4 (d, $J_{C\text{-}P}$ = 9.8 Hz), 128.5, 128.7, 128.8 (d, $J_{C\text{-}P}$ = 11.5 Hz), 129.2 (d, $J_{C\text{-}P}$ = 84.1 Hz), 131.3, 132.0 (d, $J_{C\text{-}P}$ = 103.0 Hz), 132.1, 132.56 (d, $J_{C\text{-}P}$ = 9.5 Hz), 132.59, 134.2, 141.5 (d, $J_{C\text{-}P}$ = 7.4 Hz), 141.9 (d, $J_{C\text{-}P}$ = 6.9 Hz), 150.3, 152.2. ^{31}P NMR (243 MHz, DMSO-d_6) δ 29.15 (*E*-isomer), 29.34 (*Z*-isomer). HRMS (QFT-ESI) m/z [M + Na]$^+$ Calcd for $C_{31}H_{25}NaO_3P^+$ 499.1434; Found 499.1438.

*Diphenyl(2-(((1-phenyl-2-(pyridin-2-yl)vinyl)oxy)methyl)phenyl)phosphine Oxide (**4ar**).* *Z*-isomer: a white solid, yield: 51.8 mg, 27%; R_f: 0.25 (PE:EtOAc 2:9); ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.13 (s, 2 H), 6.27 (s, 1 H), 7.00−7.04 (m, 1 H), 7.07 (dd, 1 H, J_1 = 7.4 Hz, $J_{2C\text{-}P}$ = 13.5 Hz), 7.22−7.30 (m, 4 H), 7.35−7.39 (m, 4 H), 7.41 (d, 2 H, J = 6.8 Hz,), 7.46−7.50 (m, 3 H), 7.51−7.56 (m, 4 H), 7.61 (dd, 1 H, $J_{1C\text{-}P}$ = 7.4 Hz, J_2 = 7.4 Hz), 7.92 (d, 1 H, J = 8.0 Hz), 8.01 (dd, 1 H, J_1 = 3.0 Hz, $J_{2C\text{-}P}$ = 3.6 Hz), 8.51 (s, 1 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 69.8 (d, $J_{C\text{-}P}$ = 4.4 Hz), 114.2, 120.9, 123.4, 126.7, 126.8 (d, $J_{C\text{-}P}$ = 11.7 Hz), 127.9 (d, $J_{C\text{-}P}$ = 9.8 Hz), 128.5, 128.6 (d, $J_{C\text{-}P}$ = 12.2 Hz), 128.8, 129.4 (d, $J_{C\text{-}P}$ = 100.5 Hz), 131.8 (d, $J_{C\text{-}P}$ = 9.9 Hz), 132.0 (d, $J_{C\text{-}P}$ = 1.7 Hz), 132.1 (d, $J_{C\text{-}P}$ = 102.2 Hz), 132.4, 133.2 (d, $J_{C\text{-}P}$ = 12.1 Hz), 135.4, 136.0, 142.8 (d, $J_{C\text{-}P}$ = 7.1 Hz), 149.0, 155.0, 158.1; ^{31}P NMR (243 MHz, $CDCl_3$) δ 31.18; HRMS (ESI-QFT) m/z [M + H$^+$] Calcd for $C_{32}H_{27}NO_2P^+$ 488.1774; Found 488.1778. *E*-isomer: a white solid, yield: 65.8 mg, 34%; R_f: 0.13 (PE:EtOAc 2:9); ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.41 (s, 2 H), 5.83 (s, 1 H), 6.59 (d, 1 H, J = 7.8 Hz), 6.89 (s, 1 H), 7.14 (dd, 1 H, J_1 = 7.9 Hz, $J_{2C\text{-}P}$ = 13.1 Hz), 7.20−7.25 (m, 4 H), 7.25−7.32 (m, 3 H), 7.43−7.50 (m, 4 H), 7.50−7.60 (m, 3 H), 7.64−7.70 (m, 4 H), 7.77−7.82 (m, 1 H), 8.42 (s, 1 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 68.2 (d, $J_{C\text{-}P}$ = 4.5 Hz), 104.2, 119.9, 123.9, 127.0 (d, $J_{C\text{-}P}$ = 12.4 Hz), 128.1, 128.7 (d, $J_{C\text{-}P}$ = 12.1 Hz), 128.8 (d, $J_{C\text{-}P}$ = 9.9 Hz), 128.9, 129.4, 129.7 (d, $J_{C\text{-}P}$ = 100.6 Hz), 132.01 (d, $J_{C\text{-}P}$ = 10.0 Hz), 132.04, 132.45 (d, $J_{C\text{-}P}$ = 104.0 Hz), 132.42, 133.3 (d, $J_{C\text{-}P}$ = 11.9 Hz), 135.2, 135.8, 142.0 (d, $J_{C\text{-}P}$ = 7.2 Hz), 148.9, 156.9, 159.1; ^{31}P NMR (243 MHz, $CDCl_3$) δ 31.38; HRMS (QFT-ESI) m/z [M + H]$^+$ Calcd for $C_{32}H_{27}NO_2P^+$ 488.1774; Found 488.1779. Isolated ratio: *Z*:*E* = 44:56.

*(2-(((1-(4-Bromophenyl)-2-(4-fluorophenyl)vinyl)oxy)methyl)phenyl)diphenylphosphine Oxide (**4hg**).* A white solid isolated as an inseparable *Z*/*E* mixture (*Z*:*E* = 89:11 based on integrations of two peaks at 4.96 and 5.26 of ^{1}H NMR), yield: 65.9 mg. 80%; R_f: 0.50 (PE:EtOAc 1:1). ^{1}H NMR (600 MHz, DMSO-d_6) δ: *Z*-isomer, 4.96 (s, 2 H), 6.41 (s, 1 H), 7.02 (dd, 1 H, J_1 = 8.0 Hz, $J_{2C\text{-}P}$ = 12.6 Hz), 7.07 (dd, 2 H, $J_{1C\text{-}F}$ = 7.8 Hz, J_2 = 7.8 Hz), 7.37 (d, 2 H, J = 7.5 Hz), 7.39−7.44 (m, 1 H), 7.44−7.52 (m, 10 H), 7.53−7.59 (m, 2 H), 7.60−7.65 (m, 2 H), 7.70−7.76 (m, 1 H), 7.96−8.01 (m, 1 H); *E*-isomer (part): 5.26 (s, 2 H), 5.70 (s, 1 H), 5.79−6.84 (m, 1 H), 6.93−6.98 (m, 2 H). ^{13}C NMR (151 MHz, DMSO-d_6) δ: *Z*-isomer, 68.9 (d, $J_{C\text{-}P}$ = 4.0 Hz), 112.8 (d, $J_{C\text{-}P}$ = 4.1 Hz), 115.2 (d, $J_{C\text{-}F}$ = 21.1 Hz), 121.7, 127.25 (d, $J_{C\text{-}P}$ = 11.7 Hz), 127.30 (d, $J_{C\text{-}P}$ = 7.4 Hz), 127.6, 128.8 (d, $J_{C\text{-}P}$ = 11.7 Hz), 129.2 (d, $J_{C\text{-}P}$ = 99.2 Hz), 130.3 (d, $J_{C\text{-}F}$ = 7.7 Hz), 131.3 (d, $J_{C\text{-}P}$ = 9.4 Hz), 131.4 (d, $J_{C\text{-}F}$ = 2.7 Hz), 131.5, 131.9 (d, $J_{C\text{-}P}$ = 103.0 Hz), 132.1, 132.5 (d, $J_{C\text{-}P}$ = 11.6 Hz), 132.6, 134.4, 141.6 (d, $J_{C\text{-}P}$ = 7.0 Hz), 152.4, 160.8 (d, $J_{C\text{-}F}$ = 244.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.30 (*Z*-isomer), 31.44 (*E*-isomer). HRMS (QFT-ESI) m/z [M + Na]$^+$ Calcd for $C_{33}H_{25}BrFNaO_2P^+$ 605.0652; Found 605.0655.

*(2-(((1-(4-Fluorophenyl)-2-(4-nitrophenyl)vinyl)oxy)methyl)phenyl)diphenylphosphine Oxide (**4gd**).* A white solid isolated as an inseparable *Z*/*E* mixture (*Z*:*E* = 95:5 based on integrations of two peaks at 5.07 and 5.37 of ^{1}H NMR), yield: 112.9 mg, 68%; R_f: 0.55 (PE:EtOAc 1:1). ^{1}H NMR (600 MHz, DMSO-d_6) δ: *Z*-isomer, 5.07 (s, 2 H), 6.35 (s, 1 H), 7.04 (dd, 1 H, J_1 = 7.7 Hz, $J_{2C\text{-}P}$ = 13.6 Hz), 7.19 (dd, 2 H, $J_{1C\text{-}F}$ = 8.5 Hz, J_2 = 8.5 Hz), 7.42 (dd, 1 H, J_1 = 7.3 Hz, J_2 = 7.3 Hz), 7.44−7.51 (m, 8 H), 7.52−7.57 (m, 4 H), 7.72 (dd, 1 H, J_1 = 7.5 Hz, J_2 = 7.5 Hz), 7.76 (d, 2 H, J = 8.5 Hz), 7.93 (d, 1 H, $J_{C\text{-}P}$ = 4.1 Hz), 8.05 (d, 2 H, J = 8.5 Hz); *E*-isomer (part): 5.37 (s, 2 H), 5.84 (s, 1 H), 6.97 (d, 2 H, J = 8.5 Hz), 7.11−7.15 (m, 2 H). ^{13}C NMR (151 MHz, DMSO-d_6) δ: *Z*-isomer, 69.6 (d, $J_{C\text{-}P}$ = 4.8 Hz), 110.9, 115.7 (d, $J_{C\text{-}F}$ = 21.8 Hz), 123.5, 127.5 (d, $J_{C\text{-}P}$ = 12.5 Hz), 128.1 (d, $J_{C\text{-}P}$ = 9.3 Hz), 128.7 (d, $J_{C\text{-}P}$ = 11.3 Hz), 128.8, 128.9, 129.5 (d, $J_{C\text{-}P}$ = 99.2 Hz), 131.0, 131.3 (d, $J_{C\text{-}P}$ = 9.6 Hz), 132.02 (d, $J_{C\text{-}P}$ = 102.5 Hz), 132.03, 132.6, 132.7 (d, $J_{C\text{-}P}$ = 11.7 Hz), 141.2 (d, $J_{C\text{-}P}$ = 6.8 Hz), 142.3, 145.0, 157.0, 162.6 (d, $J_{C\text{-}F}$ = 247.4 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ 31.51 (*Z*-isomer), 31.65 (*E*-isomer). HRMS (QFT-ESI) m/z [M + Na]$^+$ Calcd for $C_{33}H_{25}FNNaO_4P^+$ 572.1397; Found 572.1399.

*(2-(((1-(Furan-2-yl)-2-(4-(trifluoromethyl)phenyl)vinyl)oxy)methyl)phenyl)diphenylphosphine Oxide (**4qs**).* A white solid isolated as an inseparable *Z*/*E* mixture (*Z*:*E* = 85:15 based on integrations of two peaks at 5.18 and 5.30 of ^{1}H NMR), yield: 162.1 mg, 96%; R_f: 0.50 (PE:EtOAc 1:1). ^{1}H NMR (600 MHz, DMSO-d_6) δ: *Z*-isomer, 5.18 (s, 2 H), 6.45 (s, 1 H), 6.51 (s, 2 H), 7.04 (dd, 1 H, J_1 = 7.3 Hz, $J_{2C\text{-}P}$ = 13.2 Hz), 7.39−7.44 (m, 1 H), 7.45−7.60 (m, 12 H), 7.61−7.66 (m, 1 H), 7.68−7.75 (m, 3 H), 7.94−7.98 (m, 1 H); *E*-isomer (part): 5.30 (s, 2 H), 5.76 (s, 1 H), 6.43 (s, 1 H), 6.49 (s, 1 H), 7.13 (d, 1 H, J_1 = 7.7 Hz, $J_{2C\text{-}P}$ = 13.3 Hz),7.76−7.80 (m, 1 H). ^{13}C NMR (151 MHz, DMSO-d_6) δ: Z-isomer, 70.0 (d, $J_{C\text{-}P}$ = 4.4 Hz), 109.5 (d, $J_{C\text{-}P}$ = 10.9 Hz), 110.3 (d, $J_{C\text{-}P}$ = 9.1 Hz), 112.0 (d, $J_{C\text{-}P}$ = 11.2 Hz), 124.2 (q, $J_{C\text{-}F}$ = 271.8 Hz), 125.1 (q, $J_{C\text{-}F}$ = 3.6 Hz), 126.7 (q, $J_{C\text{-}F}$ = 31.8 Hz), 127.4 (d, $J_{C\text{-}P}$ = 11.9 Hz), 127.8 (d, $J_{C\text{-}P}$ = 9.9 Hz), 128.6, 128.8 (d, $J_{C\text{-}P}$ = 11.3 Hz), 129.3 (d, $J_{C\text{-}P}$ = 99.1 Hz), 131.3 (d, $J_{C\text{-}P}$ = 9.3 Hz), 132.0 (d, $J_{C\text{-}P}$ = 102.7 Hz), 132.1, 132.5, 132.6 (d, $J_{C\text{-}P}$ = 11.1 Hz), 138.5, 141.4 (d, $J_{C\text{-}P}$ = 6.8 Hz), 144.3 (d, $J_{C\text{-}P}$ = 7.4 Hz), 147.5, 148.9. ^{31}P NMR (243 MHz, $CDCl_3$) δ 31.50 (*Z*-isomer), 31.63 (*E*-isomer). HRMS (QFT-ESI) m/z [M + Na]$^+$ Calcd for $C_{32}H_{24}F_3NaO_3P^+$ 567.1307; Found 567.1310.

*Methyl 4-(2-((2-(Diphenylphosphoryl)benzyl)oxy)-2-(p-tolyl)vinyl)benzoate (**4jt**).* A white solid isolated as an inseparable *Z*/*E* mixture (*Z*:*E* = 93:7 based on integrations of two peaks at 5.01 and 5.29 of ^{1}H NMR), yield: 121.9 mg, 87%; R_f: 0.50 (PE:EtOAc 1:1). ^{1}H NMR (600 MHz, DMSO-d_6) δ: *Z*-isomer, 2.34 (s, 3 H), 3.85 (s, 3 H), 5.01 (s, 2 H), 6.29 (s, 1 H), 7.02 (dd, 1 H, J_1 = 7.9 Hz, $J_{2C\text{-}P}$ = 13.7 Hz), 7.15 (d, 2 H, J = 7.5 Hz), 7.35 (d, 2 H, J = 7.5 Hz), 7.41−7.50 (m, 9 H), 7.54−7.60 (m, 2 H), 7.66 (d, 2 H, J = 7.9 Hz), 7.74 (dd, 1 H, J_1 = 7.1 Hz, J_2 = 7.1 Hz), 7.79 (d, 2 H, J = 7.9 Hz), 7.97 (d, 1 H, $J_{C\text{-}P}$ = 3.8 Hz); *E*-isomer (part): 2.29 (s, 3 H), 3.79 (s, 3 H), 5.29 (s, 2 H), 5.67 (s, 1 H), 6.88 (d, 2 H, J = 7.3 Hz), 7.08 (d, 2 H, J = 7.3 Hz). ^{13}C NMR (151 MHz, DMSO-d_6) δ: *Z*-isomer, 20.8, 52.0, 69.2 (d, $J_{C\text{-}P}$ = 4.1 Hz), 111.2 (d, $J_{C\text{-}P}$ = 9.8 Hz), 126.1, 126.9, 127.3 (d, $J_{C\text{-}P}$ = 11.4 Hz), 128.2, 128.8 (d, $J_{C\text{-}P}$ = 11.4 Hz), 128.9 (d, $J_{C\text{-}P}$ = 9.5 Hz), 129.05 (d, $J_{C\text{-}P}$ =99.4 Hz), 129.13, 129.3, 131.2 (d, $J_{C\text{-}P}$ = 9.4 Hz), 131.7 (d, $J_{C\text{-}P}$ = 103.1 Hz), 131.9, 132.1, 132.61 (d, $J_{C\text{-}P}$ = 10.8 Hz), 132.64, 138.6, 140.2, 141.6 (d, $J_{C\text{-}P}$ = 6.6 Hz), 156.6, 166.0. ^{31}P NMR (243 MHz, $CDCl_3$) δ 31.40 (*E*-isomer), 31.44 (*Z*-isomer). IR (KBr, cm^{-1}) 1716 (C═O). HRMS (QFT-ESI) m/z [M + Na]$^+$ Calcd for $C_{36}H_{31}NaO_4P^+$ 581.1852; Found 581.1858.

*(2-(((((3*E*)-1-(4-Nitrophenyl)-4-phenylbuta-1,3-dien-2-yl)oxy)methyl)phenyl)diphenylphosphine Oxide (**4od**).* A yellow solid isolated as an inseparable *Z*/*E* mixture (*Z*:*E* = 48:52 based on integrations of two peaks at 5.20 and 5.37 of ^{1}H NMR), yield: 80.2 mg, 80%; R_f: 0.57 (PE:EtOAc 1:1). ^{1}H (600 MHz, DMSO-d_6) δ: *E*-isomer, 5.37 (s, 2 H), 5.83 (s, 1 H), 6.88 (d, 1 H, J = 15.8 Hz), 7.02 (d,

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1 H, J = 15.8 H), 7.15 (dd, 1 H, J_1 = 7.9 Hz, $J_{2C\text{-}P}$ = 12.9 Hz), 7.25−7.38 (m, 4 H), 7.40−7.60 (m, 11 H), 7.62−7.71 (m, 1 H), 7.72−7.78 (m, 1 H), 7.78−7.83 (m, 1 H), 8.01 (d, 2 H, J = 8.1 Hz), 8.18 (d, 2 H, J = 8.1 Hz); *Z*-isomer, 5.20 (s, 2 H), 6.29 (s, 1 H), 6.88 (d, 1 H, J = 15.7 Hz), 6.92 (d, 1 H, J = 15.7 Hz), 7.03−7.07 (m, 1 H), 7.25−7.40 (m, 4 H), 7.40−7.60 (m, 11 H), 7.62−7.72 (m, 6 H), 8.01 (m, 1 H). ^{13}C NMR (151 MHz, DMSO-d_6) δ: *E*-isomer, 67.1 (d, $J_{C\text{-}P}$ = 3.2 Hz), 104.2, 119.5, 123.6, 124.2, 128.5 (d, $J_{C\text{-}P}$ = 7.9 Hz), 128.69, 128.74, 128.8 (d, $J_{C\text{-}P}$ = 11.8 Hz), 129.27 (d, $J_{C\text{-}P}$ = 99.5 Hz), 129.29 (d, $J_{C\text{-}P}$ = 9.8 Hz), 129.5, 131.4 (d, $J_{C\text{-}P}$ = 9.5 Hz), 132.1, 132.40 (d, $J_{C\text{-}P}$ = 102.8 Hz), 132.6, 132.7 (d, $J_{C\text{-}P}$ = 13.0 Hz), 132.8, 135.9, 140.8 (d, $J_{C\text{-}P}$ = 6.9 Hz), 144.8, 145.0, 157.6; *Z*-isomer, 70.1 (d, $J_{C\text{-}P}$ = 3.8 Hz), 114.49, 114.52, 123.6, 127.1 (d, $J_{C\text{-}P}$ = 13.8 Hz), 127.4 (d, $J_{C\text{-}P}$ = 12.1 Hz), 127.7 (d, $J_{C\text{-}P}$ = 11.6 Hz), 127.8, 128.67, 128.72, 129.5, 130.4 (d, $J_{C\text{-}P}$ = 98.9 Hz), 131.3 (d, $J_{C\text{-}P}$ = 9.4 Hz), 131.6, 132.00, 132.04 (d, $J_{C\text{-}P}$ = 102.6 Hz), 132.6, 132.9 (d, $J_{C\text{-}P}$ = 11.6 Hz), 135.8, 141.6 (d, $J_{C\text{-}P}$ = 6.8 Hz), 142.1, 143.8, 154.8. ^{31}P NMR (243 MHz, DMSO-d_6) δ 28.86 (*E*-isomer), 29.32 (*Z*-isomer). HRMS (QFT-ESI) m/z [M + Na]$^+$ Calcd for $C_{35}H_{28}NNaO_4P^+$ 580.1648; Found 580.1652.

*(2-(((2-(4-Nitrophenyl)-1-(3,4,5-trimethoxyphenyl)vinyl)oxy)methyl)phenyl)diphenylphosphine Oxide (**4nd**).* A yellow solid isolated as an inseparable *Z*/*E* mixture (*Z*:*E* = 79:21 based on integrations of two peaks at 5.13 and 5.31 of ^{1}H NMR), yield: 171.4 mg, 84%; R_f: 0.25 (PE:EtOAc 1:1). ^{1}H NMR (600 MHz, DMSO-d_6) δ: *Z*-isomer, 3.72 (s, 3 H), 3.75 (s, 6 H), 5.13 (s, 2 H), 6.39 (s, 1 H), 6.84 (s, 2 H), 7.06 (dd, 1 H, J_1 = 7.9 Hz, $J_{2C\text{-}P}$ = 13.0 Hz), 7.40−7.51 (m, 8 H), 7.51−7.58 (m, 2 H), 7.60−7.70 (m, 1 H), 7.71−7.75 (m, 1 H), 7.76 (d, 2 H, J = 8.4 Hz), 7.95−8.00 (m, 1 H), 8.06 (d, 2 H, J = 8.4 Hz); *E*-isomer (part): 3.61 (s, 6 H), 3.70 (s, 3 H), 5.31 (s, 2 H), 5.75 (s, 1 H), 6.55 (s, 2 H), 7.02 (d, 2 H, J = 7.8 Hz), 7.14 (dd, 1 H, J_1 = 8.0 Hz, J_2 = 13.0 Hz). ^{13}C NMR (151 MHz, DMSO-d_6) δ: *Z*-isomer, 55.9, 60.1, 69.8 (d, $J_{C\text{-}P}$ = 3.9 Hz), 104.0 (d, $J_{C\text{-}P}$ = 5.1 Hz), 110.3 (d, $J_{C\text{-}P}$ = 8.7 Hz), 123.5, 127.4 (d, $J_{C\text{-}P}$ = 11.4 Hz), 128.1 (d, $J_{C\text{-}P}$ = 9.3 Hz), 128.7, 128.8, 129.5 (d, $J_{C\text{-}P}$ = 99.0 Hz), 130.1, 131.2 (d, $J_{C\text{-}P}$ = 9.2 Hz), 132.0, 132.1 (d, $J_{C\text{-}P}$ = 102.6 Hz), 132.5, 132.7 (d, $J_{C\text{-}P}$ = 11.7 Hz), 138.5, 141.5 (d, $J_{C\text{-}P}$ = 6.8 Hz), 142.6, 144.8, 152.9, 158.3; *E*-isomer (part): 55.8, 60.0, 67.8 (d, $J_{C\text{-}P}$ = 3.4 Hz), 101.3, 106.5 (d, $J_{C\text{-}P}$ = 9.1 Hz), 123.2, 128.9, 129.9, 130.4 (d, $J_{C\text{-}P}$ = 99.0 Hz), 131.4 (d, $J_{C\text{-}P}$ = 10.5 Hz), 132.1, 132.9 (d, $J_{C\text{-}P}$ = 11.8 Hz), 138.5, 140.7 (d, $J_{C\text{-}P}$ = 6.8 Hz), 144.31, 144.35, 152.9, 158.9. ^{31}P NMR (243 MHz, $CDCl_3$) δ 31.57 (*E*-isomer), 31.57 (*Z*-isomer, overlapped). HRMS (QFT-ESI) m/z [M + Na]$^+$ Calcd for $C_{36}H_{32}NNaO_7P^+$ 644.1809; Found 644.1812.

*(2-(((1,2-Diphenylvinyl)oxy)methyl)phenyl)diphenylphosphine Oxide (**4aa**).* A white solid isolated as an inseparable *Z*/*E* mixture (*Z*:*E* = 95:5 based on integrations of two peaks at 5.10 and 5.35 of ^{1}H NMR), yield: 124.0 mg, 85%; R_f: 0.20 (PE:EtOAc 1:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ: *Z*-isomer, 5.10 (s, 2 H), 6.04 (s, 1 H), 7.03−7.09 (m, 1 H), 7.10−7.15 (m, 1 H), 7.16−7.26 (m, 6 H), 7.30−7.38 (m, 6 H), 7.42−7.46 (m, 2 H), 7.49−7.57 (m, 6 H), 7.57−7.61 (m, 1 H), 8.05−8.10 (m, 1 H); *E*-isomer (part), 5.35 (s, 2 H), 5.65 (s, 1 H), 6.83 (d, 2 H, J = 7.2 Hz), 6.94−7.00 (m, 1 H), 7.64−7.73 (m, 4 H), 7.79−7.83 (m, 1 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ: *Z*-isomer, 69.5 (d, $J_{C\text{-}P}$ = 4.2 Hz), 113.5, 126.4, 126.5, 126.7 (d, $J_{C\text{-}P}$ = 12.7 Hz), 127.7 (d, $J_{C\text{-}P}$ = 9.7 Hz), 128.3, 128.3 (overlapped), 128.5 (d, $J_{C\text{-}P}$ = 19.0 Hz), 128.6, 128.7, 129.1 (d, $J_{C\text{-}P}$ = 101.5 Hz), 131.8 (d, $J_{C\text{-}P}$ = 9.7 Hz), 132.0 (d, $J_{C\text{-}P}$ = 1.7 Hz), 132.2 (d, $J_{C\text{-}P}$ = 102.4 Hz), 132.4, 133.1 (d, $J_{C\text{-}P}$ = 12.1 Hz), 135.8, 136.2, 143.3 (d, $J_{C\text{-}P}$ = 7.2 Hz), 155.0. ^{31}P NMR (243 MHz, $CDCl_3$) δ 31.35 (*Z*-isomer), 31.30 (*E*-isomer). HRMS (QFT-ESI) m/z [M + Na]$^+$ Calcd for $C_{33}H_{27}NaO_2P^+$ 509.1641; Found 509.1645.

*Diphenyl(2-(((1-phenyl-2-(p-tolyl)vinyl)oxy)methyl)phenyl)phosphine Oxide (**4aj**).* A white solid isolated as an inseparable *Z*/*E* mixture (*Z*:*E* = 96:4 based on integrations of two peaks at 5.09 and 5.33 of ^{1}H NMR), yield: 130.3 mg, 87%; R_f: 0.30 (PE:EtOAc 1:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ: *Z*-isomer, 2.29 (s, 3 H), 5.09 (s, 2 H), 6.04 (s, 1 H), 7.01 (d, 2 H, J = 7.8 Hz), 7.03−7.09 (m, 1 H), 7.16−7.20 (m, 3 H), 7.21−7.25 (m, 1 H), 7.30−7.37 (m, 6 H), 7.41−7.48 (m, 4 H), 7.49−7.55 (m, 4 H), 7.57−7.61 (m, 1 H), 8.06−8.10 (m, 1 H); *E*-isomer (part): 2.20 (s, 3 H), 5.33 (s, 2 H), 5.63 (s, 1 H), 6.73 (d, 2 H, J = 7.8 Hz), 6.85 (d, 2 H, J = 7.8 Hz), 7.65−7.7 (m, 4 H), 7.79−7.83 (m, 1 H). ^{31}C NMR (151 MHz, $CDCl_3$) δ: *Z*-isomer, 21.4, 69.4 (d, $J_{C\text{-}P}$ = 3.9 Hz), 113.5, 126.3, 126.6 (d, $J_{C\text{-}P}$ = 12.7 Hz), 127.7 (d, $J_{C\text{-}P}$ = 9.8 Hz), 128.1, 128.5 (d, $J_{C\text{-}P}$ = 22.8 Hz), 128.6, 129.0, 129.1 (d, $J_{C\text{-}P}$ = 101.2 Hz), 131.9 (d, $J_{C\text{-}P}$ = 9.8 Hz), 132.0 (d, $J_{C\text{-}P}$ = 1.5 Hz), 132.2 (d, $J_{C\text{-}P}$ = 103.6 Hz), 132.4, 132.9, 133.1 (d, $J_{C\text{-}P}$ = 11.9 Hz), 136.1, 136.3, 143.4 (d, $J_{C\text{-}P}$ = 7.2 Hz), 154.2. ^{31}P NMR (243 MHz, $CDCl_3$) δ 31.33 (*Z*-isomer), 31.26 (*E*-isomer). HRMS (QFT-ESI) m/z [M + Na]$^+$ Calcd for $C_{34}H_{29}NaO_2P^+$ 523.1797; Found 523.1800.

*(2-(((2-(4-Methoxyphenyl)-1-phenylvinyl)oxy)methyl)phenyl)diphenylphosphine Oxide (**4ak**).* A white solid isolated as an inseparable *Z*/*E* mixture (*Z*:*E* = 97:3 based on integrations of two peaks at 5.09 and 5.32 of ^{1}H NMR), yield: 112.3 mg, 87%; R_f: 0.40 (PE:EtOAc 1:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ: *Z*-isomer, 3.76 (s, 3 H), 5.09 (s, 2 H), 6.04 (s, 1 H), 6.74 (d, J = 8.4 Hz, 2 H), 7.03−7.09 (m, 1 H), 7.17−7.21 (m, 3 H), 7.22−7.26 (m, 1 H), 7.31−7.37 (m, 6 H), 7.42−7.47 (m, 2 H), 7.48−7.55 (m, 6 H), 7.58−7.62 (m, 1 H), 8.07−8.11 (m, 1 H); *E*-isomer (part), 3.68 (s, 3 H), 5.32 (s, 2 H), 5.61 (s, 1 H), 6.61 (d, 2 H, J = 8.4 Hz), 7.78−7.84 (m, 1 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ: *Z*-isomer, 55.2, 69.3 (d, $J_{C\text{-}P}$ = 4.4 Hz), 113.2, 113.7, 126.1, 126.6 (d, $J_{C\text{-}P}$ = 12.5 Hz), 127.6 (d, $J_{C\text{-}P}$ = 9.7 Hz), 127.9, 128.5 (d, $J_{C\text{-}P}$ = 23..3 Hz), 128.6, 129.1 (d, $J_{C\text{-}P}$ = 101.0 Hz), 129.9, 129.9 (overlapped), 131.8 (d, $J_{C\text{-}P}$ = 9.7 Hz), 132.0, 132.2 (d, $J_{C\text{-}P}$ = 105.2 Hz), 132.4, 133.1 (d, $J_{C\text{-}P}$ = 12.1 Hz), 136.3, 143.4 (d, $J_{C\text{-}P}$ = 7.1 Hz), 153.2, 158.2. ^{31}P NMR (243 MHz, $CDCl_3$) δ 31.33 (*Z*-isomer), 31.08 (*E*-isomer). HRMS (QFT-ESI) m/z [M + Na]$^+$ Calcd for $C_{34}H_{29}NaO_3P^+$ 539.1747; Found 539.1750.

*(2-(((2-(3,4-Dimethoxyphenyl)-1-phenylvinyl)oxy)methyl)phenyl)diphenylphosphine Oxide (**4al**).* A white solid isolated as an inseparable *Z*/*E* mixture (*Z*:*E* = 93:7 based on integrations of two peaks at 5.00 and 5.25 of ^{1}H NMR), yield: 109.5 mg, 81%; R_f: 0.33 (PE:EtOAc 1:1). ^{1}H NMR (600 MHz, DMSO-d_6) δ: *Z*-isomer, 3.42 (s, 3 H), 3.75 (s, 3 H), 5.00 (s, 2 H), 6.37 (s, 1 H), 6.83 (d, J = 6.9 Hz, 1 H), 7.00−7.10 (m, 2 H), 7.27−7.37 (m, 4 H), 7.38−7.51 (m, 10 H), 7.51−7.60 (m, 2 H), 7.61−7.70 (m, 1 H), 7.71−7.77 (m, 1 H), 8.10−18.14 (m, 1 H); *E*-isomer (part): 3.37 (s, 3 H), 3.65 (s, 3 H), 5.25 (s, 2 H), 5.61 (s, 1 H), 6.70 (d, 2 H, J = 6.9 Hz). ^{13}C NMR (151 MHz, DMSO-d_6) δ: *Z*-isomer, 54.8, 55.3, 68.7, 111.3, 11.4, 113.4, 121.7, 125.2, 127.1 (d, $J_{C\text{-}P}$ = 11.9 Hz), 127.2 (d, $J_{C\text{-}P}$ = 7.7 Hz), 127.9, 128.1, 128.6, 128.6 (overlapped), 128.7 (d, $J_{C\text{-}P}$ = 11.8 Hz), 129.1 (d, $J_{C\text{-}P}$ = 89.5 Hz), 131.2 (d, $J_{C\text{-}P}$ = 9.6 Hz), 131.9 (d, $J_{C\text{-}P}$ = 102.5 Hz), 132.1, 132.50, 132.53 (d, $J_{C\text{-}P}$ = 11.0 Hz), 135.5, 142.1 (d, $J_{C\text{-}P}$ = 7.0 Hz), 147.8, 148.2, 151.9. ^{31}P NMR (243 MHz, $CDCl_3$) δ 31.25 (*Z*-isomer), 31.50 (*E*-isomer). HRMS (QFT-ESI) m/z [M + Na]$^+$ Calcd for $C_{35}H_{31}NaO_4P^+$ 569.1852; Found 569.1858.

*(2-(((2-(4-Methoxyphenyl)-1-(3,4,5-trimethoxyphenyl)vinyl)oxy)methyl)phenyl)diphenylphosphine Oxide (**4nk**).* A white solid isolated as an inseparable *Z*/*E* mixture (*Z*:*E* = 91:9 based on integrations of two peaks at 5.01 and 5.19 of ^{1}H NMR), yield: 207.7 mg, 68%; R_f: 0.25 (PE:EtOAc 1:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ: *Z*-isomer, 3.71 (s, 9 H), 3.75 (s, 3 H), 5.01 (s, 2 H), 6.31 (s, 1 H), 6.76 (s, 2 H), 6.81 (d, 2 H, J = 8.8 Hz), 7.04 (dd, 1 H, J_1 = 7.5 Hz, J_2 = 13.8 Hz), 7.41 (dd, 1 H, J_1 = 7.4 Hz, J_2 = 7.5 Hz), 7.44−7.59 (m, 12 H), 7.74 (dd, 1 H, J_1 = 7.5 Hz, J_2 = 7.5 Hz), 8.07 (dd, 1 H, $J_{1C\text{-}P}$ = 3.3 Hz, J_2 = 7.5 Hz); *E*-isomer (part): 3.59 (s, 6 H), 3.67 (s, 3 H), 3.68 (s, 3 H), 5.19 (s, 2 H), 5.55 (s, 1 H). ^{13}C NMR (151 MHz, DMSO-d_6) δ: *Z*-isomer, 54.9, 55.7, 60.0, 68.8, 102.8, 112.5, 113.7, 127.06 (d, $J_{C\text{-}P}$ = 12.5 Hz), 127.07 (d, $J_{C\text{-}P}$ = 9.4 Hz), 127.8, 128.7 (d, $J_{C\text{-}P}$ = 11.7 Hz), 129.0 (d, $J_{C\text{-}P}$ = 102.4 Hz), 129.3, 129.6, 131.2 (d, $J_{C\text{-}P}$ = 9.8 Hz), 131.99 (d, $J_{C\text{-}P}$ = 102.5 Hz), 132.06, 132.52, 132.53 (d, $J_{C\text{-}P}$ = 12.5 Hz), 137.6, 142.3 (d, $J_{C\text{-}P}$ = 6.7 Hz), 152.2, 152.8, 157.9. ^{31}P NMR (162 MHz, DMSO-d_6) δ 28.57 (*E*-isomer), 29.11 (*Z*-isomer). HRMS (QFT-ESI) m/z [M + Na]$^+$ Calcd for $C_{37}H_{35}NaO_6P^+$ 629.2063; Found 629.2068.

*(2-(((3-Methyl-1-phenylbut-1-en-1-yl)oxy)methyl)phenyl)diphenylphosphine Oxide (**4ap**).* 1.2 equiv of phosphonium salt **3aa** was used. A colorless gum isolated as an inseparable *Z*/*E* mixture (*Z*:*E* = 93:7 based on integrations of two peaks at 4.89 and 5.00 of ^{1}H NMR), yield: 37.8 mg, 28%; R_f: 0.31 (PE:EtOAc 2.5:1). ^{1}H NMR (600 MHz, DMSO-d_6) δ: *Z*-isomer, 0.83 (d, 6 H, J = 6.7 Hz), 2.54−

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2.61 (m, 1 H), 4.89 (s, 2 H), 5.30 (d, 1 H, J = 9.4 Hz), 7.01 (dd, 1 H, J_1 = 7.7 Hz, $J_{2C\text{-}P}$ = 13.7 Hz), 7.24−7.29 (m, 3 H), 7.30−7.34 (m, 2 H), 7.36−7.41 (m, 1 H), 7.48−7.55 (m, 8 H), 7.60−7.64 (m, 2 H), 7.70−7.75 (m, 1 H), 7.96−7.99 (m, 1 H); *E*-isomer (part): 4.20 (d, 1 H, J = 10.1 Hz), 5.00 (s, 2 H). ^{13}C NMR (151 MHz, DMSO-d_6) δ: *Z*-isomer, 23.0, 24.8 (d, $J_{C\text{-}P}$ = 9.0 Hz), 69.8 (d, $J_{C\text{-}P}$ = 4.5 Hz), 122.7 (d, $J_{C\text{-}P}$ = 12.5 Hz), 124.9, 127.1 (d, $J_{C\text{-}P}$ = 11.7 Hz), 127.67 (d, $J_{C\text{-}P}$ = 8.9 Hz), 127.75, 128.5, 128.8 (d, $J_{C\text{-}P}$ = 11.2 Hz), 129.2 (d, $J_{C\text{-}P}$ = 100.0 Hz), 131.3 (d, $J_{C\text{-}P}$ = 9.0 Hz), 132.1, 132.2 (d, $J_{C\text{-}P}$ = 102.4 Hz), 132.5 (d, $J_{C\text{-}P}$ = 15.3 Hz), 132.6, 135.0, 142.3 (d, $J_{C\text{-}P}$ = 7.1 Hz), 150.8. ^{31}P NMR (243 MHz, DMSO-d_6) δ 28.40 (*E*-isomer), 29.23 (*Z*-isomer). HRMS (QFT-ESI) m/z [M + Na]$^+$ Calcd for $C_{30}H_{29}NaO_2P^+$ 475.1797; Found 475.1793.

*2-Isopropyl-1-phenyl-2,4-dihydro-1H-benzo[d][1,3]oxaphosphinine 1-Oxide (**14**).* The reaction of **3pa** with **2a** using *t*-BuOK as base did not produce the corresponding vinyl ether, and instead **14** was isolated in 81% (83.4 mg) yield as a mixture of two stereoisomers (79:21 determined by ^{1}H NMR based on integrations of two peaks at 3.72 and 3.62). The reaction of **3pa** with **2p** afforded **14** in 96% (115.8 mg) yield as a mixture of two stereoisomers (68:32 determined by ^{1}H NMR based on integrations of two peaks at 3.74 and 3.63). By developing four times using PE:EtOAc 1:1.5 as eluate, these two stereoisomers could be partly separated by preparative TLC (silica gel). R_f: 0.29 (minor stereoisomer), 0.24 (major stereoisomer). ^{1}H NMR (600 MHz, $CDCl_3$) δ: major stereoisomer, 0.91 (d, 3 H, J = 6.3 Hz), 1.06 (d, 3 H, J = 6.6 Hz), 1.52−1.58 (m, 1 H), 3.67 (d, 1 H, J = 9.8 Hz), 4.83 (d, 1 H, J = 15.7 Hz), 5.00 (d, 1 H, J = 15.7 Hz), 7.06−7.10 (m, 1 H), 7.24−7.29 (m, 1 H), 7.33−7.40 (m, 3 H), 7.41−7.45 (m, 1 H), 7.67 (dd, 1 H, J_1 = 8.0 Hz, $J_{2C\text{-}P}$ = 12.0 Hz), 7.70−7.75 (m, 2 H); minor stereoisomer, 0.85 (d, 3 H, J = 6.6 Hz), 1.15 (d, 3 H, J = 6.4 Hz), 2.43−2.52 (m, 1 H), 3.63 (dd, 1 H, J_1 = 9.1 Hz, $J_{2C\text{-}P}$ = 13.6 Hz), 4.86 (d, 1 H, J = 15.6 Hz), 5.15 (d, 1 H, J = 15.6 Hz), 7.18−7.22 (m, 1 H), 7.26−7.32 (m, 1 H), 7.43−7.55 (m, 5 H), 7.65−7.79 (m, 2 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ: major stereoisomer, 18.6, 19.8 (d, $J_{C\text{-}P}$ = 11.1 Hz), 29.9, 71.6 (d, $J_{C\text{-}P}$ = 1.9 Hz), 84.0 (d, $J_{C\text{-}P}$ = 84.4 Hz), 123.8 (d, $J_{C\text{-}P}$ = 8.0 Hz), 127.9 (d, $J_{C\text{-}P}$ = 11.2 Hz), 128.2 (d, $J_{C\text{-}P}$ = 11.9 Hz), 129.0 (d, $J_{C\text{-}P}$ = 93.2 Hz), 130.8 (d, $J_{C\text{-}P}$ = 96.1 Hz), 131.5 (d, $J_{C\text{-}P}$ = 5.8 Hz), 131.7, 131.9 (d, $J_{C\text{-}P}$ = 1.8 Hz), 132.4 (d, $J_{C\text{-}P}$ = 9.4 Hz), 142.1 (d, $J_{C\text{-}P}$ = 1.8 Hz); minor stereoisomer, 19.5 (d, $J_{C\text{-}P}$ = 9.2 Hz), 19.6 (d, $J_{C\text{-}P}$ = 3.2 Hz), 29.3, 71.2 (d, $J_{C\text{-}P}$ = 2.9 Hz), 85.3 (d, $J_{C\text{-}P}$ = 82.4 Hz), 124.3 (d, $J_{C\text{-}P}$ = 8.1 Hz), 127.8 (d, $J_{C\text{-}P}$ = 11.4 Hz), 128.5 (d, $J_{C\text{-}P}$ = 11.7 Hz), 128.7 (d, $J_{C\text{-}P}$ = 128.5 Hz), 131.6 (d, $J_{C\text{-}P}$ = 9.5 Hz), 131.8, 131.9, 132.5 (d, $J_{C\text{-}P}$ = 94.6 Hz), 132.6 (d, $J_{C\text{-}P}$ = 6.6 Hz), 142.0 (d, $J_{C\text{-}P}$ = 3.4 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ 19.53 (major stereoisomer), 12.74 (minor stereoisomer). HRMS (QFT-ESI) m/z [M + Na]$^+$ Calcd for $C_{17}H_{19}NaO_2P^+$ 309.1015; Found 309.1018 (major stereoisomer), 309.1016 (minor stereoisomer).

General Procedure for the Hydrolysis of Vinyl Ethers 4. A mixture of vinyl ether **4** (0.22 mmol), MeOH (4.5 mL), and 6 M HCl (1.5 mL) in a round-bottom flask (25 mL) was refluxed for 30 min. After it cooled down to rt, the mixture was evaporated to remove MeOH and extracted with CH_2Cl_2 (10 mL × 2). The combined extract was dried over anhyd MgSO4 and after evaporation isolated by preparative TLC (silica gel) to give ketone **5**.

*1,2-Diphenylethanone (**5a**).*[52] A white solid, yield: 40.5 mg, 81%; R_f: 0.77 (PE:EtOAc 3:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.27 (s, 2 H, CH_2), 7.21−7.28 (m, 3 H), 7.29−7.34 (m, 2 H), 7.41−7.46 (m, 2 H), 7.51−7.56 (m, 1 H), 8.00 (d, 2 H, J = 7.2 Hz). ^{13}C NMR (151 MHz, $CDCl_3$) δ 45.5, 126.9, 128.66, 128.70, 128.73, 129.5, 133.2, 134.6, 136.6, 197.7. IR (KBr, cm^{-1}) 1686 (C═O).

*1-Phenyl-2-(p-tolyl)ethanone (**5b**).*[53] A white solid, yield: 42.6 mg, 78%; R_f: 0.77 (PE:EtOAc 3:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.30 (s, 3 H), 4.23 (s, 2 H), 7.12 (d, 2 H, J = 6.9 Hz), 7.15 (d, 2 H, J = 6.9 Hz), 7.41−7.45 (m, 2 H), 7.50−7.55 (m, 1 H), 8.00 (d, 2 H, J = 7.2 Hz). ^{13}C NMR (151 MHz, $CDCl_3$) δ 21.1, 45.2, 128.7, 128.7 (overlapped), 129.4, 129.5, 131.5, 133.1, 136.5, 136.7, 197.9. IR (KBr, cm^{-1}) 1687 (C═O).

*2-(3,4-Dimethoxyphenyl)-1-phenylethanone (**5c**).*[53] A white solid, yield: 43.5 mg, 85%; R_f: 0.44 (PE:EtOAc 3:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.85 (s, 6 H), 4.23 (s, 2 H), 6.79 (s, 1 H), 6.82 (s, 2 H), 7.43−748 (m, 2 H), 7.53−7.57 (m, 1 H), 8.01 (d, 2 H, J = 7.8 Hz). ^{13}C NMR (151 MHz, $CDCl_3$) δ 45.1, 55.86, 55.88, 111.3, 112.5, 121.6, 127.0, 128.6, 128.7, 133.2, 136.6, 148.0, 149.0, 197.9. IR (KBr, cm^{-1}) 1677 (C═O).

*(E)-1-(4-nitrophenyl)-4-phenylbut-3-en-2-one (**5d**).*[54] A pale yellow solid, yield: 40.6 mg, 73%; R_f: 0.48 (PE:EtOAc 3:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.09 (s, 2 H), 6.80 (d, 1 H, J = 16.1 Hz), 7.39−7.45 (m, 5 H), 7.55 (d, 2 H, J = 8.3 Hz), 7.66 (d, 1 H, J = 16.1 Hz), 8.21 (d, 2 H, J = 8.3 Hz). ^{13}C NMR (151 MHz, $CDCl_3$) δ 47.4, 123.8, 124.9, 128.5, 129.0, 130.5, 131.0, 134.0, 141.9, 144.3, 147.0, 195.5. IR (KBr, cm^{-1}) 1693 (C═O).

*2-(4-Nitrophenyl)-1-(3,4,5-trimethoxyphenyl)ethanone (**5e**).*[55] A white solid, yield: 39.7 mg, 86%; R_f: 0.24 (PE:EtOAc 3:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.92 (s, 6 H), 3.94 (s, 3 H), 4.40 (s, 2 H), 7.26 (s, 2 H), 7.43 (d, 2 H, J = 8.1 Hz), 8.20 (d, 2 H, J = 8.1 Hz). ^{13}C NMR (151 MHz, $CDCl_3$) δ 44.8, 56.3, 61.0, 106.0, 123.7, 130.5, 131.2, 142.2, 143.1, 147.0, 153.1, 194.8. IR (KBr, cm^{-1}) 1685 (C═O).

*Methyl 4-(2-Oxo-2-(p-tolyl)ethyl)benzoate (**5f**).* A white solid, yield: 48.5 mg, 75%; R_f: 0.52 (PE:EtOAc 3:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.40 (s, 3 H), 3.89 (s, 3 H), 4.31 (s, 2 H), 7.25 (d, 2 H, J = 7.5 Hz), 7.33 (d, 2 H, J = 7.5 Hz), 7.90 (d, 2 H, J = 7.8 Hz), 7.99 (d, 2 H, J = 7.8 Hz). ^{13}C NMR (151 MHz, $CDCl_3$) δ 21.7, 45.3, 52.1, 128.7, 128.8, 129.4, 129.6, 129.9, 133.9, 140.1, 144.3, 166.9, 196.5. IR (KBr, cm^{-1}) 1715 (C═O of ester), 1678 (C═O of ketone). HRMS (QFT-ESI) m/z [M + Na] $^+$ Calcd for $C_{17}H_{16}NaO_3^+$ 291.0992; Found 291.0995.

*1-(Furan-2-yl)-2-(4-(trifluoromethyl)phenyl)ethanone (**5g**).* A white solid, yield: 59.8 mg, 78%; R_f: 0.50 (PE:EtOAc 3:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.19 (s, 2 H), 6.56 (s, 1 H), 7.26 (s, 1 H), 7.42 (d, J = 7.8 Hz, 2 H), 7.58 (d, J = 7.8 Hz, 2 H), 7.61 (s, 1 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 44.9, 112.6, 118.1, 124.2 (q, $J_{C\text{-}F}$ = 272.1 Hz), 125.5 (q, $J_{C\text{-}F}$ = 3.6 Hz), 129.3 (q, $J_{C\text{-}F}$ = 32.3 Hz), 130.0, 138.0, 146.9, 152.2, 185.6. IR (KBr, cm^{-1}) 1674 (C═O). HRMS (QFT-ESI) m/z [M + Na]$^+$ Calcd for $C_{13}H_9F_3NaO_2^+$ 277.0447; Found 277.0450.

*2-(4-Methoxyphenyl)-1-(3,4,5-trimethoxyphenyl)ethanone (**5h**).*[55] A white solid, yield: 52.6 mg, 98%; R_f: 0.50 (PE:EtOAc 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.79 (s, 3 H), 3.90 (s, 6 H), 3.92 (s, 3 H), 4.20 (s, 2 H), 6.88 (d, 2 H, J = 8.6 Hz), 7.20 (d, 2 H, J = 8.6 Hz), 7.27 (s, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 44.7, 55.2, 56.2, 60.9, 106.3, 114.2, 126.8, 130.2, 131.7, 142.6, 153.0, 158.5, 196.7. IR (KBr, cm^{-1}) 1677.

The One-Pot Synthesis of 5a on a Gram Scale. To a mixture of phosphonium salt **3aa** (3.045 g, 6.6 mmol), aldehyde **2a** (0.584 g, 5.5 mmol), and anhyd THF (100 mL) in a round-bottom flask (250 mL) was added *t*-BuOK (1 M in THF, 7.9 mL, 7.9 mmol) dropwise. After it was stirred at rt for 3 h, the mixture was evaporated and the residue was mixed with 6 M HCl (33 mL) and MeOH (99 mL). The mixture was refluxed for 30 min, evaporated to remove MeOH, and then extracted with PE (70 mL × 5) and EtOAc (70 mL × 2). The combined extract was evaporated and isolated by flash column chromatography (silica gel) eluted with PE:EtOAc (10:1) to give **5a** (0.581 g) in 54% yield based on aldehyde **2a**.

The ^{18}O-Labeling Experiment. ^{18}O-**2a** was prepared according to the literature procedure.[56] The phosphonium salt prepared from ^{18}O-**2a**, DPPPM **1**, and Ph_3PHBF_4 using the same procedure for **3ab** was analyzed by ^{1}H and ^{13}C NMR and HRMS, and none of them showed the formation of ^{18}O-**3ab**.

■ ASSOCIATED CONTENT

Supporting Information

NMR spectra of all cyclic α-alkoxyphosphonium salts, vinyl ethers, and ketones. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01031.

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Notes

The authors declare no competing financial interest.

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