

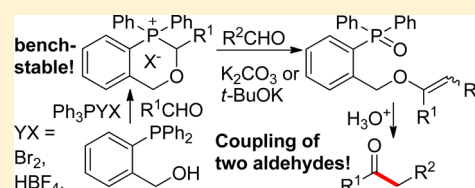
Cyclic α -Alkoxyphosphonium Salts from (2-(Diphenylphosphino)phenyl)methanol and Aldehydes and Their Application in Synthesis of Vinyl Ethers and Ketones via Wittig Olefination

Wenhua Huang,* Hong-Ying Rong, and Jie Xu

Department of Chemistry, Tianjin University, 92 Weijin Road, Tianjin 300072, P. R. China

S 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.



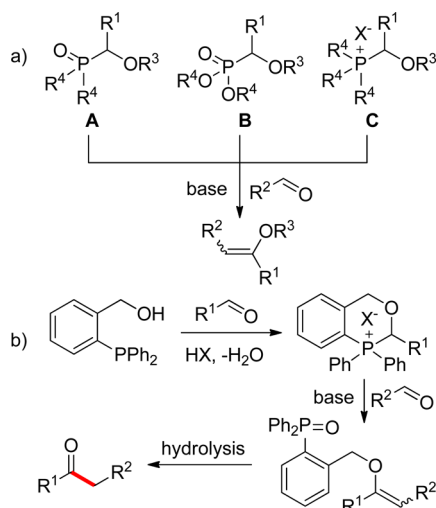
INTRODUCTION

Vinyl ethers have been widely used in not only organic synthesis^{1–7} but also polymer synthesis⁸ 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 salts²² or the reaction of

chlorodiphenylphosphine with acetal³² 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 chloride¹⁷ 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 ($< -40^\circ C$).²⁰

To overcome these limitations, we hypothesized that a cyclic α -alkoxyphosphonium salt from the reaction of (2-(diphenylphosphino)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



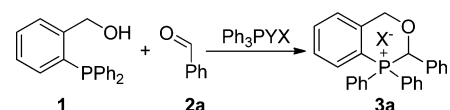
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alkoxyphosphonium salts prepared from acetals. Herein, we report our experimental results on testing this hypothesis.

RESULTS AND DISCUSSION

DPPPM **1** was readily prepared⁴¹ from the commercially available (2-diphenylphosphino)benzaldehyde by the reduction using NaBH₄. 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 Ph₃PBr 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



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	HBFe ₄	A	3ab	64
6	Br ₂	B ^d	3aa	74
7	Br ₂	B ^e	3aa	78
8	HBFe ₄	B ^e	3ab	74

^aMethod A: mixed a solution of **1** (0.86 mmol) and **2** (0.86 mmol) in 2 mL of THF with a saturated solution of Ph₃PYX in THF (12 mL for Ph₃PBr, 5 mL for Ph₃HBFe₄ and Ph₃PBr₂), rt, overnight. Method B: mixed **1**, **2**, and Ph₃PYX with a certain amount of THF, rt, overnight. ^bRefluxing for 9 h. ^cUsing 2 equiv of Ph₃PBr in THF (26 mL). ^dUsing 4 mL of THF. ^eUsing 1 mL of THF.

mixture for 9 h led to the almost same yield (entry 2). Increasing the usage of Ph₃PBr to 2 equiv reduced the yield of **3aa** to 17% (entry 3). The yield of **3aa** could be improved to 49% when using Ph₃PBr₂ instead of Ph₃PBr (entry 4). Further switching to Ph₃PHBFe₄ 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

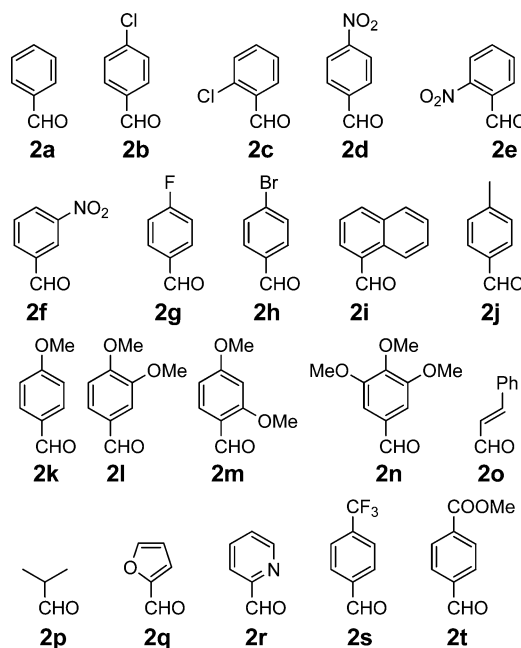
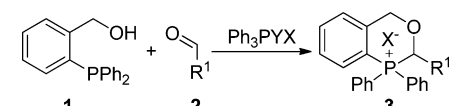


Figure 1. Aldehydes used in this work.

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



entry	YX	R ¹	3	yield ^a (%)
1	Br ₂	Ph	3aa	78
2	HBFe ₄	Ph	3ab	74
3	Br ₂	4-ClC ₆ H ₄	3ba	68
4	Br ₂	2-ClC ₆ H ₄	3ca	57
5	Br ₂	4-O ₂ NC ₆ H ₄	3da	50
6	Br ₂	2-O ₂ NC ₆ H ₄	3ea	36
7	Br ₂	3-O ₂ NC ₆ H ₄	3fa	53
8	Br ₂	4-FC ₆ H ₄	3ga	89
9	HBFe ₄	4-BrC ₆ H ₄	3hb	73
10	HBFe ₄	1-naphthyl	3ib	75
11	HBFe ₄	4-MeC ₆ H ₄	3jb	86
12	HBFe ₄	4-MeOC ₆ H ₄	3kb	81
13	HBFe ₄	3,4-(MeO) ₂ C ₆ H ₃	3 lb	89
14	HBFe ₄	2,4-(MeO) ₂ C ₆ H ₃	3mb	84
15	HBFe ₄	3,4,5-(MeO) ₃ C ₆ H ₂	3nb	82
16	HBFe ₄	(<i>E</i>)-PhCH=CH	3ob	87
17	Br ₂	<i>i</i> -Pr	3pa	63
18	Br ₂	2-furyl	3qa	64

^aReaction conditions: **1** (0.7 mmol), **2** (0.70 mmol), Ph₃PBr₂ (0.38 mmol) or Ph₃PHBFe₄ (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 K₂CO₃ as a base. When a mixture of phosphonium salt **3aa**, aldehyde **2b**, and K₂CO₃ in DMSO/CH₃CN (5/1) was stirred at room temperature overnight, **4ab** was isolated as an inseparable *Z*/

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 ₆ H ₄	4ab	61 (89:11)
2	A	Ph	4-O ₂ NC ₆ H ₄	4ad	84 (85:15)
3	A	Ph	2-O ₂ NC ₆ H ₄	4ae	75 (40:60)
4	A	Ph	4-BrC ₆ H 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 ₆ H ₄	4-FC ₆ H ₄	4hg	80 (89:11)
9	A	4-FC ₆ H ₄	4-O ₂ NC ₆ H ₄	4gd	68 (95:5)
10	A	2-Furyl	4-F ₃ CC ₆ H ₄	4qs	96 (85:15)
11	A	4-MeC ₆ H ₄	4-MeO ₂ CC ₆ H ₄	4jt	87 (93:7)
12	A	(E)-PhCH=CH	4-O ₂ NC ₆ H ₄	4od	80 (48:52)
13	A	3,4,5-(MeO) ₃ C ₆ H ₂	4-O ₂ NC ₆ H ₄	4nd	84 (79:21)
14	A	Ph	Ph	4aa	19 (90:10)
15	A	Ph	4-MeC ₆ H ₄	4aj	20 (93:7)
16	A	Ph	3,4-(MeO) ₂ C ₆ H ₃	4al	^d
17	B	Ph	Ph	4aa	85 (95:5)
18	B	Ph	4-MeC ₆ H ₄	4aj	87 (96:4)
19	B	Ph	4-MeOC ₆ H ₄	4ak	87 (97:3)
20	B	Ph	3,4-(MeO) ₂ C ₆ H ₃	4al	81 (93:7)
21	B	3,4,5-(MeO) ₃ C ₆ H ₂	4-MeOC ₆ H ₄	4nk	68 (91:9)
22	B	Ph	i-Pr	4ap	28 ^e (93:7)

^aCondition A: **2** (0.31 mmol), **3** (0.37 mmol), K₂CO₃ (0.44 mmol), DMSO (1 mL), and CH₃CN (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. ^bThe number in the parentheses is the *Z*:*E* ratio determined by ¹H NMR. ^cIsolated *Z*:*E* ratio. ^d4al was not detected. ^eUsing 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 reported¹⁹ 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 aldehyde 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 ₆ H ₄	5b	78
3	Ph	3,4-(MeO) ₂ C ₆ H ₃	5c	85
4	(E)-PhCH=CH	4-O ₂ NC ₆ H ₄	5d	73
5	3,4,5-(MeO) ₂ C ₆ H ₂	4-O ₂ NC ₆ H ₄	5e	86
6	4-MeC ₆ H ₄	4-MeO ₂ CC ₆ H ₄	5f	75
7	2-furyl	4-F ₃ CC ₆ H ₄	5g	78
8	3,4,5-(MeO) ₂ C ₆ H ₂	4-MeOC ₆ H ₄	5h	98

lethanones are useful building blocks for synthesizing a variety of heterocycles⁴³ 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 diarylethylene,⁴⁶ and by transition-metal-catalyzed carbonylative coupling reaction of benzyl halides with potassium aryltrifluoroborates.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 benzoin,⁴⁹ which is limited to symmetrical benzoin, (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 HBF₄ 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 ¹⁸O-labeling experiment in which ¹⁸O-2a and 1 were treated with Ph₃PHBF₄ 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 ¹⁸O-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 reported⁵¹ to lose a phenyl group to form alkylidiphenylphosphine oxide in the presence of *t*-BuOK or NaH. In addition, the hydrolysis of alkyltriphenylphosphonium salts under basic conditions has also been used to prepare²² alkylidiphenylphosphine oxide.

CONCLUSION

In summary, we have synthesized a variety of cyclic 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.

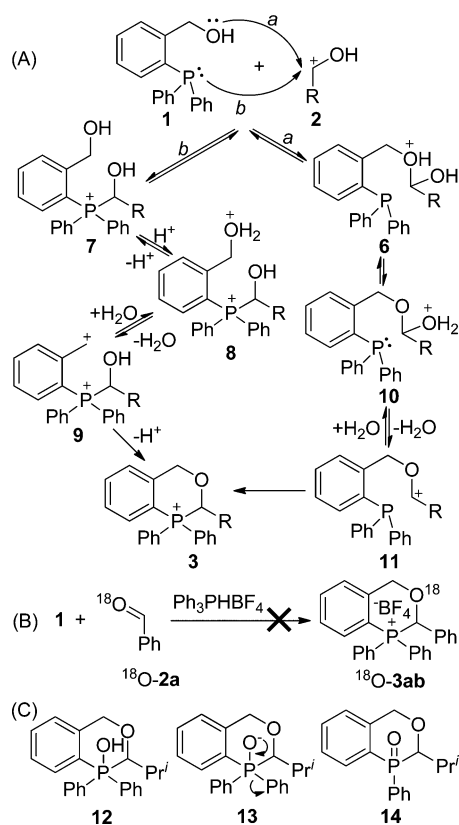
EXPERIMENTAL SECTION

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), Ph₃PBr₂ (162.5 mg, 0.38 mmol) or Ph₃PHBF₄ (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. ¹H 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-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-P} = 6.8 Hz, *J*₂ = 7.2 Hz), 7.53 (d, 1 H, *J*_{C-P} = 3.2 Hz), 7.56–7.67 (m, 4 H), 7.75 (dd, 1 H, *J*_{1C-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-P} = 12.0 Hz). ¹³C NMR (151 MHz, DMSO-*d*₆) δ 70.6, 74.4 (d, *J*_{C-P} = 55.6 Hz), 112.9 (d, *J*_{C-P} = 80.5 Hz), 113.8 (d, *J*_{C-P} = 84.7 Hz), 116.0 (d, *J*_{C-P}

Scheme 2. Formation Mechanism of Cyclic α -Alkoxyphosphonium Salts



= 79.3 Hz), 126.1 (d, J_{C-P} = 4.5 Hz), 126.6 (d, J_{C-P} = 8.6 Hz), 128.7 (d, J_{C-P} = 2.1 Hz), 129.1 (d, J_{C-P} = 11.6 Hz), 129.607, 129.609 (d, J_{C-P} = 12.4 Hz), 130.5 (d, J_{C-P} = 12.4 Hz), 131.0 (d, J_{C-P} = 2.1 Hz), 134.2 (d, J_{C-P} = 6.6 Hz), 134.8 (d, J_{C-P} = 10.0 Hz), 135.1 (d, J_{C-P} = 9.5 Hz), 135.2, 135.5, 135.8 (d, J_{C-P} = 2.0 Hz), 143.1 (d, J_{C-P} = 3.6 Hz). ^{31}P NMR (162 MHz, DMSO- d_6) δ 2.85. HRMS (MALDI-TOF) m/z [M - Br $^-$] Calcd for $\text{C}_{26}\text{H}_{22}\text{OP}^+$ 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. ^1H NMR (400 MHz, DMSO- d_6) δ 5.56 (d, 1 H, J_1 = 16.4 Hz), 5.60 (d, 1 H, J_1 = 16.4 Hz), 6.90 (d, 2 H, J_1 = 7.6 Hz), 6.96 (dd, 2 H, J_1 = 7.8 Hz, J_{2C-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-P} = 12.4 Hz). ^{13}C NMR (100 MHz, DMSO- d_6) δ 71.3, 75.3 (d, J_{C-P} = 55.1 Hz), 113.3 (d, J_{C-P} = 80.1 Hz), 114.2 (d, J_{C-P} = 84.4 Hz), 116.5 (d, J_{C-P} = 78.7 Hz), 126.6 (d, J_{C-P} = 4.4 Hz), 127.0 (d, J_{C-P} = 8.6 Hz), 129.2 (d, J_{C-P} = 2.9 Hz), 129.7 (d, J_{C-P} = 11.9 Hz), 130.1 (d, J_{C-P} = 12.5 Hz), 130.2, 131.1 (d, J_{C-P} = 12.3 Hz), 131.3 (d, J_{C-P} = 2.5 Hz), 134.6 (d, J_{C-P} = 6.7 Hz), 135.1 (d, J_{C-P} = 9.7 Hz), 135.6 (d, J_{C-P} = 9.4 Hz), 135.7, 136.0 (d, J_{C-P} = 2.5 Hz), 136.3 (d, J_{C-P} = 2.5 Hz), 143.5 (d, J_{C-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 $_4\text{B}^-$] Calcd for $\text{C}_{26}\text{H}_{22}\text{OP}^+$ 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. ^1H 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_1 = 16.4 Hz), 6.89 (dd, 2 H, J_{1C-P} = 2.2 Hz, J_2 = 8.5 Hz), 7.01 (dd, 2 H, J_1 = 7.8 Hz, J_{2C-P} = 12.6 Hz), 7.39 (d, 2 H, J_2 = 8.5 Hz), 7.45 (d, 1 H, J_{C-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-P} = 12.4 Hz). ^{13}C NMR (100 MHz, DMSO- d_6) δ 71.2 (d, J_{C-P} = 1.8 Hz), 74.2 (d, J_{C-P} = 54.8 Hz), 113.3 (d, J_{C-P} = 80.4 Hz), 114.2 (d, J_{C-P} = 83.8 Hz), 116.2 (d, J_{C-P} = 78.9 Hz), 127.1 (d, J_{C-P} = 8.8 Hz), 128.5 (d, J_{C-P} = 4.6 Hz), 129.3 (d, J_{C-P} = 2.0 Hz), 129.7 (d, J_{C-P} = 11.9 Hz), 130.3 (d, J_{C-P} = 12.5 Hz), 130.5 (d, J_{C-P} = 2.5 Hz), 131.1 (d, J_{C-P} = 12.4 Hz), 134.5 (d, J_{C-P} = 6.5 Hz), 134.8 (d, J_{C-P} = 4.1 Hz), 135.4 (d, J_{C-P} = 10.0 Hz), 135.66 (d, J_{C-P} = 9.9 Hz), 135.71, 136.1 (d, J_{C-P} = 2.2 Hz), 136.4 (d, J_{C-P} = 2.6 Hz), 143.5 (d, J_{C-P} = 3.6 Hz). ^{31}P NMR (162 MHz, DMSO- d_6) δ 3.21. HRMS (MALDI-TOF) m/z [M - Br $^-$] Calcd for $\text{C}_{26}\text{H}_{21}\text{ClOP}^+$ 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. ^1H 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_1 = 16.0 Hz), 6.66 (dd, 1 H, J_{1C-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-P} = 12.8 Hz). ^{13}C NMR (151 MHz, DMSO- d_6) δ 70.1, 73.7 (d, J_{C-P} = 55.1 Hz), 112.95 (d, J_{C-P} = 83.2 Hz), 113.02 (d, J_{C-P} = 81.8 Hz), 116.4 (d, J_{C-P} = 78.2 Hz), 126.5 (d, J_{C-P} = 8.6 Hz), 127.3 (d, J_{C-P} = 2.6 Hz), 129.2 (d, J_{C-P} = 12.2 Hz), 129.5 (d, J_{C-P} = 2.1 Hz), 129.6 (d, J_{C-P} = 3.8 Hz), 129.8 (d, J_{C-P} = 12.7 Hz), 129.9 (d, J_{C-P} = 1.5 Hz), 130.0 (d, J_{C-P} = 12.7 Hz), 130.5 (d, J_{C-P} = 5.6 Hz), 131.5 (d, J_{C-P} = 3.3 Hz), 134.4 (d, J_{C-P} = 7.1 Hz), 135.1 (d, J_{C-P} = 10.3 Hz), 135.2, 135.3 (d, J_{C-P} = 9.5 Hz), 135.57, 135.58, 143.6 (d, J_{C-P} = 3.5 Hz). ^{31}P NMR (162 MHz, DMSO- d_6) δ 3.11. HRMS (MALDI-TOF) m/z [M - Br $^-$] Calcd for $\text{C}_{26}\text{H}_{21}\text{ClOP}^+$ 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. ^1H NMR (400 MHz, DMSO- d_6) δ 5.59 (dd, 1 H, J_{1C-P} = 2.2 Hz, J_2 = 16.5 Hz), 5.66 (d, 1 H, J_{C-P} = 16.5 Hz), 6.99 (d, 2 H, J_1 = 7.6 Hz, J_{2C-P} = 12.4 Hz), 7.15 (d, 2 H, J_{1C-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-P} = 6.4 Hz, J_2 = 7.2 Hz), 7.82–7.91 (m, 3 H), 7.95 (dd, 1 H, J_{1C-P} =

7.6 Hz, J_2 = 8.4 Hz), 8.00 (dd, 1 H, J_{1C-P} = 6.8 Hz, J_2 = 8.0 Hz), 8.16 (d, 2 H, J_1 = 8.4 Hz), 8.22 (dd, 2 H, J_1 = 7.8 Hz, J_{2C-P} = 12.6 Hz). ^{13}C NMR (100 MHz, DMSO- d_6) δ 71.2, 74.3 (d, J_{C-P} = 55.5 Hz), 113.0 (d, J_{C-P} = 81.8 Hz), 113.8 (d, J_{C-P} = 84.4 Hz), 115.9 (d, J_{C-P} = 79.4 Hz), 124.4, 127.2 (d, J_{C-P} = 9.1 Hz), 128.0, 129.8 (d, J_{C-P} = 11.7 Hz), 130.4 (d, J_{C-P} = 12.1 Hz), 131.2 (d, J_{C-P} = 12.2 Hz), 134.6 (d, J_{C-P} = 6.0 Hz), 135.6 (d, J_{C-P} = 11.3 Hz), 135.7 (d, J_{C-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 $\text{C}_{26}\text{H}_{21}\text{NO}_3\text{P}^+$ 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. ^1H NMR (400 MHz, DMSO- d_6) δ 5.51 (dd, 1 H, J_{1C-P} = 2.0 Hz, J_2 = 16.0 Hz), 5.72 (d, 1 H, J_{C-P} = 16.0 Hz), 7.10 (d, 1 H, J_{C-P} = 7.6 Hz), 7.18 (d, 2 H, J_1 = 7.6 Hz, J_{2C-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-P} = 7.2 Hz, J_2 = 7.6 Hz), 7.87–7.94 (m, 2 H), 8.00 (dd, 1 H, J_1 = 8.0 Hz), 8.11 (dd, 2 H, J_1 = 7.6 Hz, J_{2C-P} = 12.8 Hz). ^{13}C NMR (100 MHz, DMSO- d_6) δ 70.7 (d, J_{C-P} = 3.8 Hz), 74.2 (d, J_{C-P} = 52.7 Hz), 113.6 (d, J_{C-P} = 56.3 Hz), 114.5 (d, J_{C-P} = 57.4 Hz), 117.9 (d, J_{C-P} = 79.0 Hz), 125.6 (d, J_{C-P} = 2.0 Hz), 127.33 (d, J_{C-P} = 1.6 Hz), 127.34 (d, J_{C-P} = 8.4 Hz), 129.87 (d, J_{C-P} = 11.9 Hz), 129.90 (d, J_1 = 4.7 Hz), 130.3 (d, J_{C-P} = 12.7 Hz), 130.5 (d, J_{C-P} = 12.7 Hz), 131.5 (d, J_{C-P} = 2.9 Hz), 134.5 (d, J_{C-P} = 2.7 Hz), 134.8 (d, J_{C-P} = 4.8 Hz), 134.9 (d, J_{C-P} = 10.1 Hz), 135.55, 135.60 (d, J_{C-P} = 9.6 Hz Hz), 135.7 (d, J_{C-P} = 3.0 Hz), 136.0 (d, J_{C-P} = 2.9 Hz), 144.0 (d, J_{C-P} = 3.6 Hz), 146.9 (d, J_{C-P} = 5.2 Hz). ^{31}P NMR (243 MHz, DMSO- d_6) δ 4.96. HRMS (MALDI-TOF) m/z [M - Br $^-$] Calcd for $\text{C}_{26}\text{H}_{21}\text{NO}_3\text{P}^+$ 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. ^1H NMR (400 MHz, DMSO- d_6) δ 5.60 (dd, 1 H, J_{1C-P} = 2.0 Hz, J_2 = 16.4 Hz), 5.86 (d, 1 H, J_{C-P} = 16.4 Hz), 7.01 (d, 2 H, J_1 = 7.8 Hz, J_{2C-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-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-P} = 7.2 Hz, J_2 = 7.2 Hz), 8.22 (d, 1 H, J_1 = 8.0 Hz), 8.29 (s, 1 H), 8.42 (dd, 2 H, J_1 = 8.0 Hz, J_{2C-P} = 12.0 Hz). ^{13}C NMR (100 MHz, DMSO- d_6) δ 71.2, 73.7 (d, J_{C-P} = 55.0 Hz), 112.9 (d, J_{C-P} = 81.3 Hz), 114.0 (d, J_{C-P} = 83.7 Hz), 115.6 (d, J_{C-P} = 79.2 Hz), 121.4 (d, J_{C-P} = 4.4 Hz), 124.9 (d, J_{C-P} = 2.9 Hz), 127.1 (d, J_{C-P} = 8.7 Hz), 129.7 (d, J_{C-P} = 12.1 Hz), 130.3 (d, J_{C-P} = 12.6 Hz), 131.1 (overlapped), 131.2 (d, J_{C-P} = 12.4 Hz), 133.1 (d, J_{C-P} = 4.2 Hz), 133.6 (d, J_{C-P} = 2.2 Hz), 134.5 (d, J_{C-P} = 7.0 Hz), 135.5 (d, J_{C-P} = 10.1 Hz), 135.7 (d, J_{C-P} = 9.6 Hz), 135.8 (d, J_{C-P} = 1.7 Hz), 136.2 (d, J_{C-P} = 2.6 Hz), 136.5 (d, J_{C-P} = 2.3 Hz), 143.4 (d, J_{C-P} = 3.6 Hz), 147.9 (d, J_{C-P} = 3.3 Hz). ^{31}P NMR (162 MHz, DMSO- d_6) δ 4.06. HRMS (MALDI-TOF) m/z [M - Br $^-$] Calcd for $\text{C}_{26}\text{H}_{21}\text{NO}_3\text{P}^+$ 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. ^1H NMR (400 MHz, DMSO- d_6) δ 5.54 (dd, 1 H, J_{1C-P} = 2.0 Hz, J_2 = 16.3 Hz), 5.72 (dd, 1 H, J_{1C-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-P} = 55.7 Hz), 113.3 (d, J_{C-P} = 80.1 Hz), 114.2 (d, J_{C-P} = 84.0 Hz), 116.27 (d, J_{C-P} = 79.0 Hz), 116.33 (d, J_{1C-P} = 2.4 Hz, J_{2C-F} = 22.0 Hz), 127.1 (d, J_{C-P} = 8.8 Hz), 127.7, 129.0 (dd, J_{1C-P} = 4.7 Hz, J_{2C-F} = 8.6 Hz), 129.7 (d, J_{C-P} = 11.9 Hz), 130.2 (d, J_{C-P} = 12.6 Hz), 131.1 (d, J_{C-P} = 12.3 Hz), 134.5 (d, J_{C-P} = 6.5 Hz), 135.3 (d, J_{C-P} = 9.9 Hz), 135.7 (d, J_{C-P} = 9.4 Hz), 135.7 (overlapped), 136.0 (d, J_{C-P} = 2.8 Hz), 136.3 (d, J_{C-P} = 2.7 Hz), 143.5 (d, J_{C-P} = 3.7 Hz), 163.0 (dd, J_{1C-P} = 3.8 Hz, J_{2C-F} = 247.0 Hz). ^{31}P NMR (243 MHz, DMSO- d_6) δ 2.94. HRMS (MALDI-TOF) m/z [M - Br $^-$] Calcd for $\text{C}_{26}\text{H}_{21}\text{FOP}^+$ 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. ^1H NMR (400 MHz, DMSO- d_6) δ 5.61 (s, 2 H), 6.86 (d, 2 H, J_1 = 7.6 Hz), 7.01 (dd, 2 H, J_1 = 8.0 Hz, J_{2C-P} = 12.0 Hz), 7.35 (d, 1 H, J_{C-P} = 2.8 Hz), 7.54 (d, 2 H, J_1 = 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

(dd, 2 H, $J_1 = 8.0$ Hz, $J_{2C-P} = 12.0$ Hz). ^{13}C NMR (100 MHz, DMSO- d_6) δ 71.4, 74.7 (d, $J_{C-P} = 55.9$ Hz), 113.2 (d, $J_{C-P} = 80.8$ Hz), 114.1 (d, $J_{C-P} = 84.2$ Hz), 116.1 (d, $J_{C-P} = 78.8$ Hz), 123.6 (d, $J_{C-P} = 4.4$ Hz), 127.1 (d, $J_{C-P} = 8.7$ Hz), 128.7 (d, $J_{C-P} = 4.6$ Hz), 129.7 (d, $J_{C-P} = 11.8$ Hz), 130.3 (d, $J_{C-P} = 12.7$ Hz), 130.7 (d, $J_{C-P} = 2.6$ Hz), 131.2 (d, $J_{C-P} = 12.3$ Hz), 132.3 (d, $J_{C-P} = 2.5$ Hz), 134.6 (d, $J_{C-P} = 6.7$ Hz), 135.2 (d, $J_{C-P} = 9.9$ Hz), 135.7 (d, $J_{C-P} = 9.6$ Hz), 135.7 (overlapped), 136.2 (d, $J_{C-P} = 2.3$ Hz), 136.4 (d, $J_{C-P} = 2.9$ Hz), 143.5 (d, $J_{C-P} = 3.7$ 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 [$M - \text{F}_4\text{B}^-$] Calcd for $\text{C}_{26}\text{H}_{21}\text{BrOP}^+$ 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. ^1H NMR (600 MHz, DMSO- d_6) δ 5.63 (d, 1 H, $J = 16.2$ Hz), 5.79 (d, 1 H, $J_{C-P} = 16.2$ 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, $J_{C-P} = 54.8$ Hz), 113.2 (d, $J_{C-P} = 80.2$ Hz), 114.1 (d, $J_{C-P} = 83.1$ Hz), 116.9 (d, $J_{C-P} = 77.1$ Hz), 123.6, 125.5 (d, $J_{C-P} = 3.2$ Hz), 127.1 (d, $J_{C-P} = 8.5$ Hz), 126.5, 126.7, 127.3 (d, $J_{C-P} = 3.0$ Hz), 127.4 (d, $J_{C-P} = 6.1$ Hz), 129.3, 129.5 (d, $J_{C-P} = 3.8$ Hz), 129.7 (d, $J_{C-P} = 12.0$ Hz), 130.1 (d, $J_{C-P} = 12.4$ Hz), 130.7 (d, $J_{C-P} = 12.7$ Hz), 130.8 (d, $J_{C-P} = 5.0$ Hz), 133.6 (d, $J_{C-P} = 2.0$ Hz), 135.09 (d, $J_{C-P} = 5.6$ Hz), 135.11 (d, $J_{C-P} = 10.3$ Hz), 135.83, 135.84 (d, $J_{C-P} = 9.0$ Hz), 135.9, 136.1 (d, $J_{C-P} = 2.4$ Hz), 144.2 (d, $J_{C-P} = 3.6$ 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 [$M - \text{F}_4\text{B}^-$] Calcd for $\text{C}_{30}\text{H}_{24}\text{OP}^+$ 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. ^1H 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, $J_{C-P} = 56.1$ Hz), 112.9 (d, $J_{C-P} = 80.5$ Hz), 113.8 (d, $J_{C-P} = 85.0$ Hz), 116.0 (d, $J_{C-P} = 79.4$ Hz), 126.2, 126.5 (d, $J_{C-P} = 4.8$ Hz), 127.7 (d, $J_{C-P} = 2.3$ Hz), 129.1 (d, $J_{C-P} = 11.4$ Hz), 129.3, 129.6 (d, $J_{C-P} = 12.5$ Hz), 130.6 (d, $J_{C-P} = 12.0$ Hz), 134.1, 134.6 (d, $J_{C-P} = 9.4$ Hz), 135.18, 135.21 (d, $J_{C-P} = 8.8$ Hz), 135.5, 135.7, 139.4 (d, $J_{C-P} = 3.4$ Hz), 143.0 (d, $J_{C-P} = 3.8$ 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 [$M - \text{F}_4\text{B}^-$] Calcd for $\text{C}_{27}\text{H}_{24}\text{OP}^+$ 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. ^1H 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, $J_{1C-P} = 2.0$ 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, $J_{2C-P} = 12.2$ Hz), 7.24 (d, 1 H, $J = 5.6$ Hz), 7.59–7.70 (m, 4 H), 7.75 (dd, 1 H, $J_{1C-P} = 6.4$ Hz, $J_{2C-P} = 7.2$ 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, $J_{2C-P} = 12.2$ Hz). ^{13}C NMR (100 MHz, DMSO- d_6) δ 55.8, 71.5, 75.1 (d, $J_{C-P} = 56.4$ Hz), 113.5 (d, $J_{C-P} = 79.0$ Hz), 114.4 (d, $J_{C-P} = 84.5$ Hz), 114.7 (d, $J_{C-P} = 1.9$ Hz), 116.6 (d, $J_{C-P} = 78.8$ Hz), 122.9 (d, $J_{C-P} = 2.5$ Hz), 127.1 (d, $J_{C-P} = 8.7$ Hz), 128.3 (d, $J_{C-P} = 4.6$ Hz), 129.7 (d, $J_{C-P} = 11.8$ Hz), 130.2 (d, $J_{C-P} = 12.5$ Hz), 131.1 (d, $J_{C-P} = 12.2$ Hz), 134.6 (d, $J_{C-P} = 6.0$ Hz), 135.1 (d, $J_{C-P} = 9.6$ Hz), 135.7, 135.8 (d, $J_{C-P} = 9.4$ Hz), 136.0 (d, $J_{C-P} = 2.2$ Hz), 136.3 (d, $J_{C-P} = 1.9$ Hz), 143.6 (d, $J_{C-P} = 3.7$ Hz), 160.7 (d, $J_{C-P} = 3.1$ 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 [$M - \text{F}_4\text{B}^-$] Calcd for $\text{C}_{27}\text{H}_{24}\text{O}_2\text{P}^+$ 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. ^1H 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, $J_{2C-P} = 12.2$ 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, $J_{1C-P} = 3.3$ 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, $J_{2C-P} = 12.4$ Hz). ^{13}C NMR (151 MHz, DMSO- d_6) δ 54.8, 55.5 (d, $J_{C-P} = 9.7$ Hz), 70.1, 74.7 (d, $J_{C-P} = 56.8$ Hz), 109.2, 111.5, 113.0 (d, $J_{C-P} = 79.3$ Hz), 114.2 (d, $J_{C-P} = 85.0$ Hz), 116.0 (d, $J_{C-P} = 80.0$ Hz), 119.2, 122.4, 126.5 (d, $J_{C-P} = 10.0$ Hz), 129.1 (d, $J_{C-P} = 11.3$ Hz), 129.7 (d, $J_{C-P} = 12.5$ Hz), 130.5 (d, $J_{C-P} = 11.0$ Hz), 134.1 (d, $J_{C-P} = 5.0$ Hz), 134.7 (d, $J_{C-P} = 10.0$ Hz), 135.2, 135.37 (d, $J_{C-P} = 8.8$ Hz), 135.39, 135.7, 143.1 (d, $J_{C-P} = 3.6$ Hz), 148.5 (d, $J_{C-P} = 1.8$ Hz), 149.7 (d, $J_{C-P} = 3.5$ 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 [$M - \text{F}_4\text{B}^-$] Calcd for $\text{C}_{28}\text{H}_{26}\text{O}_2\text{P}^+$ 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. ^1H 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, $J_{1C-P} = 2.2$ Hz, $J_2 = 8.6$ Hz), 6.56 (s, 1 H), 7.06 (dd, 2 H, $J_1 = 8.0$ Hz, $J_{2C-P} = 11.6$ Hz), 7.21 (d, 1 H, $J = 5.6$ Hz), 7.52 (dd, 1 H, $J_1 = 7.8$ Hz, $J_{2C-P} = 13.0$ 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, $J_{2C-P} = 12.6$ Hz). ^{13}C NMR (100 MHz, DMSO- d_6) δ 55.1, 55.9, 71.2, 72.6 (d, $J_{C-P} = 55.1$ Hz), 98.4 (d, $J_{C-P} = 1.3$ Hz), 106.1, 111.7 (d, $J_{C-P} = 2.5$ Hz), 114.2 (d, $J_{C-P} = 78.6$ Hz), 114.5 (d, $J_{C-P} = 83.3$ Hz), 118.1 (d, $J_{C-P} = 78.4$ Hz), 127.0 (d, $J_{C-P} = 8.6$ Hz), 129.0 (d, $J_{C-P} = 4.1$ Hz), 129.5 (d, $J_{C-P} = 11.6$ Hz), 130.0 (d, $J_{C-P} = 12.3$ Hz), 130.2 (d, $J_{C-P} = 12.5$ Hz), 134.8 (d, $J_{C-P} = 6.9$ Hz), 134.9 (d, $J_{C-P} = 13.0$ Hz), 135.42, 135.45, 135.50 (d, $J_{C-P} = 9.4$ Hz), 135.7 (d, $J_{C-P} = 2.5$ Hz), 144.0 (d, $J_{C-P} = 3.7$ Hz), 156.6 (d, $J_{C-P} = 4.2$ Hz), 162.0 (d, $J_{C-P} = 3.0$ 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 [$M - \text{F}_4\text{B}^-$] Calcd for $\text{C}_{28}\text{H}_{26}\text{O}_3\text{P}^+$ 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. ^1H 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, $J_{C-P} = 2.0$ Hz), 6.98 (dd, 2 H, $J_1 = 7.8$ Hz, $J_{2C-P} = 12.2$ 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, $J_{2C-P} = 12.4$ Hz). ^{13}C NMR (151 MHz, DMSO- d_6) δ 55.5, 60.3, 70.8 (d, $J_{C-P} = 1.5$ Hz), 75.0 (d, $J_{C-P} = 56.2$ Hz), 103.4, 112.6 (d, $J_{C-P} = 79.9$ Hz), 114.1 (d, $J_{C-P} = 84.9$ Hz), 115.9 (d, $J_{C-P} = 80.3$ Hz), 125.9 (d, $J_{C-P} = 2.7$ Hz), 126.6 (d, $J_{C-P} = 9.4$ Hz), 129.2 (d, $J_{C-P} = 11.2$ Hz), 129.6 (d, $J_{C-P} = 12.4$ Hz), 130.5 (d, $J_{C-P} = 12.2$ Hz), 134.2 (d, $J_{C-P} = 6.3$ Hz), 134.8 (d, $J_{C-P} = 9.8$ Hz), 135.2 (overlapped), 135.3 (d, $J_{C-P} = 8.8$ Hz), 135.6, 135.7, 138.2 (d, $J_{C-P} = 3.9$ Hz), 143.0 (d, $J_{C-P} = 3.2$ Hz), 152.9 (d, $J_{C-P} = 3.2$ 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 [$M - \text{F}_4\text{B}^-$] Calcd for $\text{C}_{29}\text{H}_{28}\text{O}_4\text{P}^+$ 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. ^1H 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, $J_{1C-P} = 8.1$ 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, $J_{2C-P} = 11.4$ Hz). ^{13}C NMR (100 MHz, DMSO- d_6) δ 70.5 (d, $J_{C-P} = 2.5$ Hz), 74.4 (d, $J_{C-P} = 57.8$ Hz), 113.2 (d, $J_{C-P} = 79.7$ Hz), 115.7 (d, $J_{C-P} = 81.7$ Hz), 116.6 (d, $J_{C-P} = 77.2$ Hz), 118.3 (d, $J_{C-P} = 4.1$ Hz), 127.1 (d, $J_{C-P} = 8.7$ Hz), 127.4 (d, $J_{C-P} = 1.1$ Hz), 129.2, 129.4, 129.6 (d, $J_{C-P} = 11.8$ Hz), 130.4 (d, $J_{C-P} = 12.6$ Hz), 131.0 (d, $J_{C-P} = 12.2$ Hz), 134.4 (d, $J_{C-P} = 6.2$ Hz), 134.9 (d, $J_{C-P} = 9.6$ Hz), 135.3 (d, $J_{C-P} = 3.4$ Hz), 135.6, 135.7 (d, $J_{C-P} = 9.9$ Hz), 135.9 (d, $J_{C-P} = 2.8$ Hz), 136.1 (d, $J_{C-P} = 2.6$

Hz), 136.7 (d, J_{C-P} = 12.1 Hz), 143.5 (d, J_{C-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 [$\text{M} - \text{F}_4\text{B}^-$] Calcd for $\text{C}_{28}\text{H}_{24}\text{OP}^+$ 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. ^1H 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-P} = 8.8 Hz), 7.46 (dd, 1 H, J_1 = 8.0 Hz, J_{2C-P} = 13.6 Hz), 7.55 (ddd, 1 H, J_{1C-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-P} = 12.2 Hz). ^{13}C NMR (151 MHz, DMSO- d_6) δ 18.3 (dd, J_{1C-P} = 2.2 Hz, J_{2C-P} = 11.4 Hz), 19.2 (d, J_{C-P} = 1.2 Hz), 30.1 (d, J_{C-P} = 5.6 Hz), 70.6 (ddd, J_{1C-P} = 2.3 Hz, J_{2C-P} = 9.5 Hz, J_{3C-P} = 10.4 Hz), 78.0 (dd, J_{1C-P} = 6.4 Hz, J_{2C-P} = 55.2 Hz), 113.9 (d, J_{C-P} = 8.4 Hz), 114.6 (d, J_{C-P} = 82.3 Hz), 118.1 (d, J_{C-P} = 76.0 Hz), 126.2 (d, J_{C-P} = 4.8 Hz), 129.0 (d, J_{C-P} = 11.0 Hz), 130.4 (d, J_{C-P} = 11.6 Hz), 133.6 (d, J_{C-P} = 5.6 Hz), 134.2 (d, J_{C-P} = 9.8 Hz), 134.7 (d, J_{C-P} = 2.1 Hz), 135.1 (d, J_{C-P} = 10.1 Hz), 135.4 (d, J_{C-P} = 2.0 Hz), 143.0 (d, J_{C-P} = 2.1 Hz). ^{31}P NMR (162 MHz, DMSO- d_6) δ 1.81. HRMS (MALDI-TOF) m/z [$\text{M} - \text{Br}^-$] Calcd for $\text{C}_{23}\text{H}_{24}\text{OP}^+$ 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. ^1H NMR (400 MHz, DMSO- d_6) δ 5.45 (dd, 1 H, J_{1C-P} = 2.0 Hz, J_2 = 16.4 Hz), 5.55 (d, 1 H, J_{C-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-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-P} = 12.6 Hz). ^{13}C NMR (151 MHz, DMSO- d_6) δ 69.6 (d, J_{C-P} = 60.6 Hz), 70.2 (d, J_{C-P} = 2.4 Hz), 111.3, 112.1 (overlapped), 112.4 (d, J_{C-P} = 80.8 Hz), 115.4 (d, J_{C-P} = 83.7 Hz), 116.1 (d, J_{C-P} = 84.0 Hz), 126.7 (d, J_{C-P} = 8.3 Hz), 129.1 (d, J_{C-P} = 12.1 Hz), 129.9 (d, J_{C-P} = 12.5 Hz), 130.4 (d, J_{C-P} = 12.2 Hz), 133.9 (d, J_{C-P} = 6.5 Hz), 134.6 (d, J_{C-P} = 13.0 Hz), 134.7 (d, J_{C-P} = 10.7 Hz), 135.2, 135.5, 135.7, 142.9 (d, J_{C-P} = 3.3 Hz), 143.7 (d, J_{C-P} = 4.1 Hz), 145.0. ^{31}P NMR (243 MHz, DMSO- d_6) δ -0.71. HRMS (MALDI-TOF) m/z [$\text{M} - \text{Br}^-$] Calcd for $\text{C}_{24}\text{H}_{20}\text{O}_2\text{P}^+$ 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 $\times$ 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 $t\text{-BuOK}$ 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 $t\text{-BuOK}$ (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 ^1H NMR), yield: 160.4 mg, 61%; R_f 0.50 (PE:EtOAc 1:1). ^1H 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-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-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-P} = 7.1 Hz), 112.4, 126.4, 127.8 (d, J_{C-P} = 12.1 Hz), 128.1 (d, J_{C-P} = 9.7 Hz), 128.8, 129.1, 129.2, 129.3 (d, J_{C-P} = 11.8 Hz), 129.9 (d, J_{C-P} = 90.8 Hz), 130.4, 131.4, 131.8 (d, J_{C-P} = 9.7 Hz), 132.58, 132.62 (d, J_{C-P} = 107.2 Hz), 133.0, 133.1 (d, J_{C-P} = 6.5 Hz), 134.6, 135.6, 142.3 (d,

J_{C-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 [$\text{M} + \text{Na}^+$] Calcd for $\text{C}_{33}\text{H}_{26}\text{ClNaO}_2\text{P}^+$ 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 ^1H NMR), yield: 179.6 mg, 84%; R_f 0.53 (PE:EtOAc 1:1). ^1H 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-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-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-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-P} = 4.8 Hz), 111.0, 123.6, 126.9, 127.1 (d, J_{C-P} = 12.6 Hz), 128.0 (d, J_{C-P} = 9.7 Hz), 128.5, 128.6, 128.7 (d, J_{C-P} = 10.8 Hz), 129.3, 129.6 (d, J_{C-P} = 100.4 Hz), 131.8 (d, J_{C-P} = 9.8 Hz), 132.0, 132.1 (d, J_{C-P} = 102.9 Hz), 132.4, 133.3 (d, J_{C-P} = 12.2 Hz), 135.2, 142.4 (d, J_{C-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 [$\text{M} + \text{Na}^+$] Calcd for $\text{C}_{33}\text{H}_{26}\text{NNaO}_4\text{P}^+$ 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 ^1H NMR), yield: 158.7 mg, 75%; R_f 0.53 (PE:EtOAc 1:1). ^1H 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-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-P} = 4.6 Hz), 99.7, 124.3, 126.9, 127.0 (d, J_{C-P} = 12.8 Hz), 128.0, 128.4 (d, J_{C-P} = 10.1 Hz), 128.5, 128.7 (d, J_{C-P} = 12.1 Hz), 129.4 (d, J_{C-P} = 100.9 Hz), 129.5, 130.4, 131.9, 131.9 (overlapped), 132.1 (d, J_{C-P} = 8.9 Hz), 132.5, 132.7 (d, J_{C-P} = 100.7 Hz), 133.2 (d, J_{C-P} = 12.1 Hz), 133.5, 135.0, 141.9 (d, J_{C-P} = 7.2 Hz), 148.3, 157.4; Z-isomer (part): 70.4 (d, J_{C-P} = 4.6 Hz), 106.9, 126.4, 126.82, 126.84 (d, J_{C-P} = 11.9 Hz), 128.1 (d, J_{C-P} = 11.0 Hz), 128.6 (d, J_{C-P} = 12.3 Hz), 128.8, 129.0, 129.6 (d, J_{C-P} = 100.5 Hz), 129.7, 131.7, 131.8 (d, J_{C-P} = 9.8 Hz), 132.2 (d, J_{C-P} = 103.3 Hz), 132.25, 133.1 (d, J_{C-P} = 12.2 Hz), 132.34, 135.3, 142.4 (d, J_{C-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 [$\text{M} + \text{Na}^+$] Calcd for $\text{C}_{33}\text{H}_{26}\text{NNaO}_4\text{P}^+$ 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 ^1H NMR), yield: 158.6 mg, 70%; R_f 0.58 (PE:EtOAc 1:1). ^1H 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-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-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-P} = 5.1 Hz), 112.0 (d, J_{C-P} = 4.2 Hz), 119.5, 125.8, 127.3 (d, J_{C-P} = 12.9 Hz), 127.5 (d, J_{C-P} = 9.6 Hz), 128.6, 128.7, 128.8 (d, J_{C-P} = 11.8 Hz), 129.3 (d, J_{C-P} = 91.9 Hz), 130.2, 131.2, 131.3 (d, J_{C-P} = 9.7 Hz), 132.0 (d, J_{C-P} = 102.4 Hz), 132.1, 132.56 (d, J_{C-P} = 9.2 Hz), 132.59, 134.4, 135.0, 141.7 (d, J_{C-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 [$\text{M} + \text{Na}^+$] Calcd for $\text{C}_{33}\text{H}_{26}\text{BrNaO}_2\text{P}^+$ 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 ^1H NMR), yield: 91.4 mg, 45%; R_f 0.51 (PE:EtOAc 1:1). ^1H 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

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, $J_{\text{C-P}} = 4.3$ Hz), 115.0, 123.2, 125.1, 126.2, 127.38 (d, $J_{\text{C-P}} = 10.3$ Hz), 127.41, 128.4, 128.5 (d, $J_{\text{C-P}} = 9.4$ Hz), 128.7, 128.8 (d, $J_{\text{C-P}} = 11.9$ Hz), 129.6 (d, $J_{\text{C-P}} = 99.4$ Hz), 131.3 (d, $J_{\text{C-P}} = 9.5$ Hz), 131.5, 132.1, 132.3 (d, $J_{\text{C-P}} = 10.2$ Hz), 132.5, 132.6 (d, $J_{\text{C-P}} = 10.8$ Hz), 132.7, 134.5, 137.3, 142.0 (d, $J_{\text{C-P}} = 7.1$ 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 $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{35}\text{H}_{29}\text{NaO}_2\text{P}^+$ 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 ^1H NMR), yield: 152.6 mg, 80%; R_f : 0.47 (PE:EtOAc 1:1). ^1H 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, $J_{2\text{C-P}} = 12.8$ 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, $J_{\text{C-P}} = 3.1$ Hz); *E*-isomer (part): 5.28 (s, 2 H), 5.52 (s, 1 H), 5.57 (s, 1 H), 6.25 (s, 1 H), 7.11 (dd, 1 H, $J_{\text{C-P}} = 8.1$ Hz, $J_{2\text{C-P}} = 12.8$), 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, $J_{\text{C-P}} = 10.0$ Hz), 108.9 (d, $J_{\text{C-P}} = 12.3$ Hz), 112.0 (d, $J_{\text{C-P}} = 12.4$ Hz), 125.4, 127.2 (d, $J_{\text{C-P}} = 12.1$ Hz), 127.4 (d, $J_{\text{C-P}} = 9.8$ Hz), 128.5, 128.7, 128.8 (d, $J_{\text{C-P}} = 11.5$ Hz), 129.2 (d, $J_{\text{C-P}} = 84.1$ Hz), 131.3, 132.0 (d, $J_{\text{C-P}} = 103.0$ Hz), 132.1, 132.56 (d, $J_{\text{C-P}} = 9.5$ Hz), 132.59, 134.2, 141.5 (d, $J_{\text{C-P}} = 7.4$ Hz), 141.9 (d, $J_{\text{C-P}} = 6.9$ 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 $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{31}\text{H}_{25}\text{NaO}_3\text{P}^+$ 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); ^1H 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, $J_{2\text{C-P}} = 13.5$ 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, $J_{1\text{C-P}} = 7.4$ 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, $J_{2\text{C-P}} = 3.6$ Hz), 8.51 (s, 1 H); ^{13}C NMR (151 MHz, CDCl_3) δ 69.8 (d, $J_{\text{C-P}} = 4.4$ Hz), 114.2, 120.9, 123.4, 126.7, 126.8 (d, $J_{\text{C-P}} = 11.7$ Hz), 127.9 (d, $J_{\text{C-P}} = 9.8$ Hz), 128.5, 128.6 (d, $J_{\text{C-P}} = 12.2$ Hz), 128.8, 129.4 (d, $J_{\text{C-P}} = 100.5$ Hz), 131.8 (d, $J_{\text{C-P}} = 9.9$ Hz), 132.0 (d, $J_{\text{C-P}} = 1.7$ Hz), 132.1 (d, $J_{\text{C-P}} = 102.2$ Hz), 132.4, 133.2 (d, $J_{\text{C-P}} = 12.1$ Hz), 135.4, 136.0, 142.8 (d, $J_{\text{C-P}} = 7.1$ Hz), 149.0, 155.0, 158.1; ^{31}P NMR (243 MHz, CDCl_3) δ 31.18; HRMS (ESI-QFT) m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{32}\text{H}_{27}\text{NO}_2\text{P}^+$ 488.1774; Found 488.1778. *E*-isomer: a white solid, yield: 65.8 mg, 34%; R_f : 0.13 (PE:EtOAc 2:9); ^1H 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, $J_{2\text{C-P}} = 13.1$ 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, $J_{\text{C-P}} = 4.5$ Hz), 104.2, 119.9, 123.9, 127.0 (d, $J_{\text{C-P}} = 12.4$ Hz), 128.1, 128.7 (d, $J_{\text{C-P}} = 12.1$ Hz), 128.8 (d, $J_{\text{C-P}} = 9.9$ Hz), 128.9, 129.4, 129.7 (d, $J_{\text{C-P}} = 100.6$ Hz), 132.01 (d, $J_{\text{C-P}} = 10.0$ Hz), 132.04, 132.45 (d, $J_{\text{C-P}} = 104.0$ Hz), 132.42, 133.3 (d, $J_{\text{C-P}} = 11.9$ Hz), 135.2, 135.8, 142.0 (d, $J_{\text{C-P}} = 7.2$ Hz), 148.9, 156.9, 159.1; ^{31}P NMR (243 MHz, CDCl_3) δ 31.38; HRMS (QFT-ESI) m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{32}\text{H}_{27}\text{NO}_2\text{P}^+$ 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 ^1H NMR), yield: 65.9 mg, 80%; R_f : 0.50 (PE:EtOAc 1:1). ^1H 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, $J_{2\text{C-P}} = 12.6$ Hz), 7.07 (dd, 2 H, $J_{1\text{C-F}} = 7.8$ 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, $J_{\text{C-P}} = 4.0$ Hz), 112.8 (d, $J_{\text{C-P}} = 4.1$ Hz), 115.2 (d, $J_{\text{C-F}} = 21.1$ Hz), 121.7, 127.25 (d, $J_{\text{C-P}} = 11.7$ Hz), 127.30 (d, $J_{\text{C-P}} = 7.4$ Hz), 127.6, 128.8 (d, $J_{\text{C-P}} = 11.7$ Hz), 129.2 (d, $J_{\text{C-P}} = 99.2$ Hz), 130.3 (d, $J_{\text{C-F}} = 7.7$ Hz),

131.3 (d, $J_{\text{C-P}} = 9.4$ Hz), 131.4 (d, $J_{\text{C-F}} = 2.7$ Hz), 131.5, 131.9 (d, $J_{\text{C-P}} = 103.0$ Hz), 132.1, 132.5 (d, $J_{\text{C-P}} = 11.6$ Hz), 132.6, 134.4, 141.6 (d, $J_{\text{C-P}} = 7.0$ Hz), 152.4, 160.8 (d, $J_{\text{C-F}} = 244.8$ Hz). ^{31}P NMR (162 MHz, CDCl_3) δ 31.30 (*Z*-isomer), 31.44 (*E*-isomer). HRMS (QFT-ESI) m/z $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{33}\text{H}_{25}\text{BrFNaO}_2\text{P}^+$ 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 ^1H NMR), yield: 112.9 mg, 68%; R_f : 0.55 (PE:EtOAc 1:1). ^1H 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, $J_{2\text{C-P}} = 13.6$ Hz), 7.19 (dd, 2 H, $J_{1\text{C-F}} = 8.5$ 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, $J_{\text{C-P}} = 4.1$ 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, $J_{\text{C-P}} = 4.8$ Hz), 110.9, 115.7 (d, $J_{\text{C-F}} = 21.8$ Hz), 123.5, 127.5 (d, $J_{\text{C-P}} = 12.5$ Hz), 128.1 (d, $J_{\text{C-P}} = 9.3$ Hz), 128.7 (d, $J_{\text{C-P}} = 11.3$ Hz), 128.8, 128.9, 129.5 (d, $J_{\text{C-P}} = 99.2$ Hz), 131.0, 131.3 (d, $J_{\text{C-P}} = 9.6$ Hz), 132.02 (d, $J_{\text{C-P}} = 102.5$ Hz), 132.03, 132.6, 132.7 (d, $J_{\text{C-P}} = 11.7$ Hz), 141.2 (d, $J_{\text{C-P}} = 6.8$ Hz), 142.3, 145.0, 157.0, 162.6 (d, $J_{\text{C-F}} = 247.4$ Hz). ^{31}P NMR (243 MHz, CDCl_3) δ 31.51 (*Z*-isomer), 31.65 (*E*-isomer). HRMS (QFT-ESI) m/z $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{33}\text{H}_{25}\text{FNNaO}_4\text{P}^+$ 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 ^1H NMR), yield: 162.1 mg, 96%; R_f : 0.50 (PE:EtOAc 1:1). ^1H 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, $J_{2\text{C-P}} = 13.2$ 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, $J_{2\text{C-P}} = 13.3$ Hz), 7.76–7.80 (m, 1 H). ^{13}C NMR (151 MHz, DMSO- d_6) δ : *Z*-isomer, 70.0 (d, $J_{\text{C-P}} = 4.4$ Hz), 109.5 (d, $J_{\text{C-P}} = 10.9$ Hz), 110.3 (d, $J_{\text{C-P}} = 9.1$ Hz), 112.0 (d, $J_{\text{C-P}} = 11.2$ Hz), 124.2 (q, $J_{\text{C-F}} = 271.8$ Hz), 125.1 (q, $J_{\text{C-F}} = 3.6$ Hz), 126.7 (q, $J_{\text{C-F}} = 31.8$ Hz), 127.4 (d, $J_{\text{C-P}} = 11.9$ Hz), 127.8 (d, $J_{\text{C-P}} = 9.9$ Hz), 128.6, 128.8 (d, $J_{\text{C-P}} = 11.3$ Hz), 129.3 (d, $J_{\text{C-P}} = 99.1$ Hz), 131.3 (d, $J_{\text{C-P}} = 9.3$ Hz), 132.0 (d, $J_{\text{C-P}} = 102.7$ Hz), 132.1, 132.5, 132.6 (d, $J_{\text{C-P}} = 11.1$ Hz), 138.5, 141.4 (d, $J_{\text{C-P}} = 6.8$ Hz), 144.3 (d, $J_{\text{C-P}} = 7.4$ 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 $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{32}\text{H}_{24}\text{F}_3\text{NaO}_3\text{P}^+$ 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 ^1H NMR), yield: 121.9 mg, 87%; R_f : 0.50 (PE:EtOAc 1:1). ^1H 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, $J_{2\text{C-P}} = 13.7$ 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, $J_{\text{C-P}} = 3.8$ 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, $J_{\text{C-P}} = 4.1$ Hz), 111.2 (d, $J_{\text{C-P}} = 9.8$ Hz), 126.1, 126.9, 127.3 (d, $J_{\text{C-P}} = 11.4$ Hz), 128.2, 128.8 (d, $J_{\text{C-P}} = 11.4$ Hz), 128.9 (d, $J_{\text{C-P}} = 9.5$ Hz), 129.05 (d, $J_{\text{C-P}} = 99.4$ Hz), 129.13, 129.3, 131.2 (d, $J_{\text{C-P}} = 9.4$ Hz), 131.7 (d, $J_{\text{C-P}} = 103.1$ Hz), 131.9, 132.1, 132.61 (d, $J_{\text{C-P}} = 10.8$ Hz), 132.64, 138.6, 140.2, 141.6 (d, $J_{\text{C-P}} = 6.6$ 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 $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{36}\text{H}_{31}\text{NaO}_4\text{P}^+$ 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 ^1H NMR), yield: 80.2 mg, 80%; R_f : 0.57 (PE:EtOAc 1:1). ^1H (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,

1 H, $J = 15.8$ Hz), 7.15 (dd, 1 H, $J_1 = 7.9$ Hz, $J_{2C-P} = 12.9$ 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, $J_{C-P} = 3.2$ Hz), 104.2, 119.5, 123.6, 124.2, 128.5 (d, $J_{C-P} = 7.9$ Hz), 128.69, 128.74, 128.8 (d, $J_{C-P} = 11.8$ Hz), 129.27 (d, $J_{C-P} = 99.5$ Hz), 129.29 (d, $J_{C-P} = 9.8$ Hz), 129.5, 131.4 (d, $J_{C-P} = 9.5$ Hz), 132.1, 132.40 (d, $J_{C-P} = 102.8$ Hz), 132.6, 132.7 (d, $J_{C-P} = 13.0$ Hz), 132.8, 135.9, 140.8 (d, $J_{C-P} = 6.9$ Hz), 144.8, 145.0, 157.6; Z-isomer, 70.1 (d, $J_{C-P} = 3.8$ Hz), 114.49, 114.52, 123.6, 127.1 (d, $J_{C-P} = 13.8$ Hz), 127.4 (d, $J_{C-P} = 12.1$ Hz), 127.7 (d, $J_{C-P} = 11.6$ Hz), 127.8, 128.67, 128.72, 129.5, 130.4 (d, $J_{C-P} = 98.9$ Hz), 131.3 (d, $J_{C-P} = 9.4$ Hz), 131.6, 132.00, 132.04 (d, $J_{C-P} = 102.6$ Hz), 132.6, 132.9 (d, $J_{C-P} = 11.6$ Hz), 135.8, 141.6 (d, $J_{C-P} = 6.8$ 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 $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{35}\text{H}_{28}\text{NNaO}_4\text{P}^+$ 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 ^1H NMR), yield: 171.4 mg, 84%; R_f : 0.25 (PE:EtOAc 1:1). ^1H 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, $J_{2C-P} = 13.0$ 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, $J_{C-P} = 3.9$ Hz), 104.0 (d, $J_{C-P} = 5.1$ Hz), 110.3 (d, $J_{C-P} = 8.7$ Hz), 123.5, 127.4 (d, $J_{C-P} = 11.4$ Hz), 128.1 (d, $J_{C-P} = 9.3$ Hz), 128.7, 128.8, 129.5 (d, $J_{C-P} = 99.0$ Hz), 130.1, 131.2 (d, $J_{C-P} = 9.2$ Hz), 132.0, 132.1 (d, $J_{C-P} = 102.6$ Hz), 132.5, 132.7 (d, $J_{C-P} = 11.7$ Hz), 138.5, 141.5 (d, $J_{C-P} = 6.8$ Hz), 142.6, 144.8, 152.9, 158.3; E-isomer (part): 55.8, 60.0, 67.8 (d, $J_{C-P} = 3.4$ Hz), 101.3, 106.5 (d, $J_{C-P} = 9.1$ Hz), 123.2, 128.9, 129.9, 130.4 (d, $J_{C-P} = 99.0$ Hz), 131.4 (d, $J_{C-P} = 10.5$ Hz), 132.1, 132.9 (d, $J_{C-P} = 11.8$ Hz), 138.5, 140.7 (d, $J_{C-P} = 6.8$ 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 $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{36}\text{H}_{32}\text{NNaO}_7\text{P}^+$ 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 ^1H NMR), yield: 124.0 mg, 85%; R_f : 0.20 (PE:EtOAc 1:1). ^1H 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, $J_{C-P} = 4.2$ Hz), 113.5, 126.4, 126.5, 126.7 (d, $J_{C-P} = 12.7$ Hz), 127.7 (d, $J_{C-P} = 9.7$ Hz), 128.3, 128.3 (overlapped), 128.5 (d, $J_{C-P} = 19.0$ Hz), 128.6, 128.7, 129.1 (d, $J_{C-P} = 101.5$ Hz), 131.8 (d, $J_{C-P} = 9.7$ Hz), 132.0 (d, $J_{C-P} = 1.7$ Hz), 132.2 (d, $J_{C-P} = 102.4$ Hz), 132.4, 133.1 (d, $J_{C-P} = 12.1$ Hz), 135.8, 136.2, 143.3 (d, $J_{C-P} = 7.2$ Hz), 155.0. ^{31}P NMR (243 MHz, CDCl_3) δ : 31.35 (Z-isomer), 31.30 (E-isomer). HRMS (QFT-ESI) m/z $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{33}\text{H}_{27}\text{NaO}_2\text{P}^+$ 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 ^1H NMR), yield: 130.3 mg, 87%; R_f : 0.30 (PE:EtOAc 1:1). ^1H 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). ^{13}C NMR (151 MHz, CDCl_3) δ : Z-isomer, 21.4, 69.4 (d, $J_{C-P} = 3.9$ Hz), 113.5, 126.3, 126.6 (d, $J_{C-P} = 12.7$ Hz), 127.7 (d, $J_{C-P} = 9.8$ Hz), 128.1, 128.5 (d, $J_{C-P} = 22.8$ Hz), 128.6, 129.0, 129.1 (d, $J_{C-P} = 101.2$ Hz), 131.9 (d, $J_{C-P} = 9.8$ Hz), 132.0 (d, $J_{C-P} = 1.5$ Hz), 132.2 (d, $J_{C-P} = 103.6$ Hz), 132.4, 132.9, 133.1 (d, $J_{C-P} = 11.9$ Hz), 136.1, 136.3, 143.4 (d, $J_{C-P} = 7.2$ Hz), 154.2. ^{31}P NMR (243 MHz, CDCl_3) δ : 31.33 (Z-isomer), 31.26 (E-isomer). HRMS (QFT-ESI) m/z $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{34}\text{H}_{29}\text{NaO}_2\text{P}^+$ 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 ^1H NMR), yield: 112.3 mg, 87%; R_f : 0.40 (PE:EtOAc 1:1). ^1H 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, $J_{C-P} = 4.4$ Hz), 113.2, 113.7, 126.1, 126.6 (d, $J_{C-P} = 12.5$ Hz), 127.6 (d, $J_{C-P} = 9.7$ Hz), 127.9, 128.5 (d, $J_{C-P} = 23.3$ Hz), 128.6, 129.1 (d, $J_{C-P} = 101.0$ Hz), 129.9, 129.9 (overlapped), 131.8 (d, $J_{C-P} = 9.7$ Hz), 132.0, 132.2 (d, $J_{C-P} = 105.2$ Hz), 132.4, 133.1 (d, $J_{C-P} = 12.1$ Hz), 136.3, 143.4 (d, $J_{C-P} = 7.1$ 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 $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{34}\text{H}_{29}\text{NaO}_3\text{P}^+$ 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 ^1H NMR), yield: 109.5 mg, 81%; R_f : 0.33 (PE:EtOAc 1:1). ^1H 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), 8.10–8.14 (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, $J_{C-P} = 11.9$ Hz), 127.2 (d, $J_{C-P} = 7.7$ Hz), 127.9, 128.1, 128.6, 128.6 (overlapped), 128.7 (d, $J_{C-P} = 11.8$ Hz), 129.1 (d, $J_{C-P} = 89.5$ Hz), 131.2 (d, $J_{C-P} = 9.6$ Hz), 131.9 (d, $J_{C-P} = 102.5$ Hz), 132.1, 132.50, 132.53 (d, $J_{C-P} = 11.0$ Hz), 135.5, 142.1 (d, $J_{C-P} = 7.0$ 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 $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{35}\text{H}_{31}\text{NaO}_4\text{P}^+$ 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 ^1H NMR), yield: 207.7 mg, 68%; R_f : 0.25 (PE:EtOAc 1:1). ^1H 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, $J_{1C-P} = 3.3$ 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, $J_{C-P} = 12.5$ Hz), 127.07 (d, $J_{C-P} = 9.4$ Hz), 127.8, 128.7 (d, $J_{C-P} = 11.7$ Hz), 129.0 (d, $J_{C-P} = 102.4$ Hz), 129.3, 129.6, 131.2 (d, $J_{C-P} = 9.8$ Hz), 131.99 (d, $J_{C-P} = 102.5$ Hz), 132.06, 132.52, 132.53 (d, $J_{C-P} = 12.5$ Hz), 137.6, 142.3 (d, $J_{C-P} = 6.7$ 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 $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{37}\text{H}_{35}\text{NaO}_6\text{P}^+$ 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 ^1H NMR), yield: 37.8 mg, 28%; R_f : 0.31 (PE:EtOAc 2.5:1). ^1H NMR (600 MHz, DMSO- d_6) δ : Z-isomer, 0.83 (d, 6 H, $J = 6.7$ Hz), 2.54–

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, $J_{2C-P} = 13.7$ 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, $J_{C-P} = 9.0$ Hz), 69.8 (d, $J_{C-P} = 4.5$ Hz), 122.7 (d, $J_{C-P} = 12.5$ Hz), 124.9, 127.1 (d, $J_{C-P} = 11.7$ Hz), 127.67 (d, $J_{C-P} = 8.9$ Hz), 127.75, 128.5, 128.8 (d, $J_{C-P} = 11.2$ Hz), 129.2 (d, $J_{C-P} = 100.0$ Hz), 131.3 (d, $J_{C-P} = 9.0$ Hz), 132.1, 132.2 (d, $J_{C-P} = 102.4$ Hz), 132.5 (d, $J_{C-P} = 15.3$ Hz), 132.6, 135.0, 142.3 (d, $J_{C-P} = 7.1$ 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 $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{30}\text{H}_{29}\text{NaO}_2\text{P}^+$ 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 ^1H 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 ^1H 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). ^1H 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, $J_{2C-P} = 12.0$ 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, $J_{2C-P} = 13.6$ 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, $J_{C-P} = 11.1$ Hz), 29.9, 71.6 (d, $J_{C-P} = 1.9$ Hz), 84.0 (d, $J_{C-P} = 84.4$ Hz), 123.8 (d, $J_{C-P} = 8.0$ Hz), 127.9 (d, $J_{C-P} = 11.2$ Hz), 128.2 (d, $J_{C-P} = 11.9$ Hz), 129.0 (d, $J_{C-P} = 93.2$ Hz), 130.8 (d, $J_{C-P} = 96.1$ Hz), 131.5 (d, $J_{C-P} = 5.8$ Hz), 131.7, 131.9 (d, $J_{C-P} = 1.8$ Hz), 132.4 (d, $J_{C-P} = 9.4$ Hz), 142.1 (d, $J_{C-P} = 1.8$ Hz); minor stereoisomer, 19.5 (d, $J_{C-P} = 9.2$ Hz), 19.6 (d, $J_{C-P} = 3.2$ Hz), 29.3, 71.2 (d, $J_{C-P} = 2.9$ Hz), 85.3 (d, $J_{C-P} = 82.4$ Hz), 124.3 (d, $J_{C-P} = 8.1$ Hz), 127.8 (d, $J_{C-P} = 11.4$ Hz), 128.5 (d, $J_{C-P} = 11.7$ Hz), 128.7 (d, $J_{C-P} = 128.5$ Hz), 131.6 (d, $J_{C-P} = 9.5$ Hz), 131.8, 131.9, 132.5 (d, $J_{C-P} = 94.6$ Hz), 132.6 (d, $J_{C-P} = 6.6$ Hz), 142.0 (d, $J_{C-P} = 3.4$ Hz). ^{31}P NMR (243 MHz, CDCl_3) δ 19.53 (major stereoisomer), 12.74 (minor stereoisomer). HRMS (QFT-ESI) m/z $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{17}\text{H}_{19}\text{NaO}_2\text{P}^+$ 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 $\times$ 2). The combined extract was dried over anhyd MgSO_4 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). ^1H 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 ($\text{C}=\text{O}$).

1-Phenyl-2-(*p*-tolyl)ethanone (5b).⁵³ A white solid, yield: 42.6 mg, 78%; R_f : 0.77 (PE:EtOAc 3:1). ^1H 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 ($\text{C}=\text{O}$).

2-(3,4-Dimethoxyphenyl)-1-phenylethanone (5c).⁵³ A white solid, yield: 43.5 mg, 85%; R_f : 0.44 (PE:EtOAc 3:1). ^1H 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),

7.43–7.48 (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 ($\text{C}=\text{O}$).

(*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). ^1H 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 ($\text{C}=\text{O}$).

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). ^1H 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 ($\text{C}=\text{O}$).

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). ^1H 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 ($\text{C}=\text{O}$ of ester), 1678 ($\text{C}=\text{O}$ of ketone). HRMS (QFT-ESI) m/z $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{17}\text{H}_{16}\text{NaO}_3^+$ 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). ^1H 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, $J_{C-F} = 272.1$ Hz), 125.5 (q, $J_{C-F} = 3.6$ Hz), 129.3 (q, $J_{C-F} = 32.3$ Hz), 130.0, 138.0, 146.9, 152.2, 185.6. IR (KBr, cm^{-1}) 1674 ($\text{C}=\text{O}$). HRMS (QFT-ESI) m/z $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{13}\text{H}_9\text{F}_3\text{NaO}_2^+$ 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). ^1H 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 $\times$ 5) and EtOAc (70 mL $\times$ 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 ^1H 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.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: huangwh@tju.edu.cn.

Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Dehli, J. R.; Legros, J.; Bolm, C. *Chem. Commun. (Cambridge, U.K.)* **2005**, 973.
- (2) Ousset, J. B.; Mioskowski, C.; Yang, Y. L.; Falck, J. R. *Tetrahedron Lett.* **1984**, 25, S903.
- (3) Friesen, R. W. *J. Chem. Soc., Perkin Trans. 1* **2001**, 1969.
- (4) Hiersemann, M.; Abraham, L. *Eur. J. Org. Chem.* **2002**, 1461.
- (5) Nasveschuk, C. G.; Rovis, T. *Org. Biomol. Chem.* **2008**, 6, 240.
- (6) Tokunaga, M.; Aoyama, H.; Obora, Y.; Tsuji, Y. *Recent Res. Dev. Org. Chem.* **2005**, 9, 147.
- (7) Zhu, Z.-B.; Kirsch, S. F. *Chem. Commun. (Cambridge, U.K.)* **2013**, 49, 2272.
- (8) Kanazawa, A.; Kanaoka, S.; Aoshima, S. *Chem. Lett.* **2010**, 39, 1232.
- (9) Winterheimer, D. J.; Shade, R. E.; Merlic, C. A. *Synthesis* **2010**, 2497.
- (10) Earnshaw, C.; Wallis, C. J.; Warren, S. J. *Chem. Soc., Perkin Trans. 1* **1979**, 3099.
- (11) Mukai, K.; Urabe, D.; Kasuya, S.; Aoki, N.; Inoue, M. *Angew. Chem., Int. Ed.* **2013**, 52, S300.
- (12) Chakravarty, M.; Srinivas, B.; Muthiah, C.; Swamy, K. C. K. *Synthesis* **2003**, 2368.
- (13) Jung, M. E.; Cordova, J.; Murakami, M. *Org. Lett.* **2009**, 11, 3882.
- (14) Kluge, A. F.; Cloudsdale, I. S. *J. Org. Chem.* **1979**, 44, 4847.
- (15) Schultz, A. G.; Napier, J. J.; Ravichandran, R. *J. Org. Chem.* **1983**, 48, 3408.
- (16) Colton, I. J.; Yin, D.; Grochulski, P.; Kazlauskas, R. J. *Adv. Synth. Catal.* **2011**, 353, 2529.
- (17) Roeschlaub, C. A.; Sammes, P. G. *J. Chem. Soc., Perkin Trans. 1* **2000**, 2243.
- (18) Turan, I. S.; Akkaya, E. U. *Org. Lett.* **2014**, 16, 1680.
- (19) Das, P.; McNulty, J. *Eur. J. Org. Chem.* **2010**, 3587.
- (20) Lambert, W. T.; Hanson, G. H.; Benayoud, F.; Burke, S. D. *J. Org. Chem.* **2005**, 70, 9382.
- (21) Levine, S. G. *J. Am. Chem. Soc.* **1958**, 80, 6150.
- (22) Ley, S. V.; Lygo, B.; Organ, H. M.; Wonnacott, A. *Tetrahedron* **1985**, 41, 3825.
- (23) Robert Coulsen, D. *Tetrahedron Lett.* **1964**, 5, 3323.
- (24) Brioché, J. C. R.; Barker, T. A.; Whatrup, D. J.; Barker, M. D.; Harrity, J. P. A. *Org. Lett.* **2010**, 12, 4832.
- (25) Dunkel, R.; Hoffmann, H. M. R. *Tetrahedron* **1999**, 55, 8385.
- (26) Lieberknecht, A.; Griesser, H.; Kramer, B.; Bravo, R. D.; Colinas, P. A.; Grigera, R. J. *Tetrahedron* **1999**, 55, 6475.
- (27) Meek, S. J.; Demont, E. H.; Harrity, J. P. A. *Tetrahedron Lett.* **2007**, 48, 4165.
- (28) Meek, S. J.; Pradaux, F.; Carbery, D. R.; Demont, E. H.; Harrity, J. P. A. *J. Org. Chem.* **2005**, 70, 10046.
- (29) Queron, E.; Lett, R. *Tetrahedron Lett.* **2004**, 45, 4527.
- (30) McNulty, J.; Keskar, K. *Eur. J. Org. Chem.* **2011**, 6902.
- (31) McNulty, J.; Keskar, K.; Crankshaw, D. J.; Holloway, A. C. *Bioorg. Med. Chem. Lett.* **2014**, 24, 4586.
- (32) Maleki, M.; Miller, A.; Lever, O. W., Jr. *Tetrahedron Lett.* **1981**, 22, 365.
- (33) Oehme, H.; Leissring, E. *Tetrahedron* **1981**, 37, 753.
- (34) Livantsov, M. V.; Prishchenko, A. A.; Lutsenko, I. F. *Zh. Obshch. Khim.* **1986**, 56, 94.
- (35) Kruse, C. G.; Poels, E. K.; Van der Gen, A. J. *Org. Chem.* **1979**, 44, 2911.
- (36) Dunkel, R.; Treu, J.; Martin, H.; Hoffmann, R. *Tetrahedron: Asymmetry* **1999**, 10, 1539.
- (37) Fujioka, H.; Goto, A.; Otake, K.; Kubo, O.; Sawama, Y.; Maegawa, T. *Chem. Commun. (Cambridge, U.K.)* **2011**, 47, 9894.
- (38) Goto, A.; Otake, K.; Kubo, O.; Sawama, Y.; Maegawa, T.; Fujioka, H. *Chem.—Eur. J.* **2012**, 18, 11423.
- (39) Tuckmantel, W.; Oshima, K.; Utimoto, K. *Tetrahedron Lett.* **1986**, 27, S617.
- (40) Epstein, W. W.; Garrossian, M. *Phosphorous Sulfur Relat. Elem.* **1988**, 35, 349.
- (41) Landvatter, E. F.; Rauchfuss, T. B. *Organometallics* **1982**, 1, 506.
- (42) McNulty, J.; Keskar, K. *Tetrahedron Lett.* **2008**, 49, 7054.
- (43) Kim, Y.-W.; Brueggemeier, R. W. *Tetrahedron Lett.* **2002**, 43, 6113.
- (44) Churrua, F.; SanMartin, R.; Tellitu, I.; Domínguez, E. *Org. Lett.* **2002**, 4, 1591.
- (45) Wilkinson, M. C.; Saez, F.; Hon, W. L. *Synlett* **2006**, 1063.
- (46) Liang, S.; Hammond, G. B.; Xu, B. *Chem. Commun. (Cambridge, U.K.)* **2015**, 51, 903.
- (47) Wu, X.-F.; Neumann, H.; Beller, M. *Adv. Synth. Catal.* **2011**, 353, 788.
- (48) Angle, S. R.; Neitzel, M. L. *J. Org. Chem.* **2000**, 65, 6458.
- (49) Cutulic, S. P. Y.; Findlay, N. J.; Zhou, S.-Z.; Chrystal, E. J. T.; Murphy, J. A. *J. Org. Chem.* **2009**, 74, 8713.
- (50) Farago, J.; Kotschy, A. *Synthesis* **2009**, 85.
- (51) Ngwendson, J. N.; Schultze, C. M.; Bollinger, J. W.; Banerjee, A. *Can. J. Chem.* **2008**, 86, 668.
- (52) Xu, M.-L.; Huang, W. *Tetrahedron Lett.* **2014**, 55, 4230.
- (53) Churrua, F.; SanMartin, R.; Carril, M.; Tellitu, I.; Dominguez, E. *Tetrahedron* **2004**, 60, 2393.
- (54) Kale, A. P.; Pawar, G. G.; Kapur, M. *Org. Lett.* **2012**, 14, 1808.
- (55) Wu, M.; Sun, Q.; Yang, C.; Chen, D.; Ding, J.; Chen, Y.; Lin, L.; Xie, Y. *Bioorg. Med. Chem. Lett.* **2007**, 17, 869.
- (56) Baraniak, J.; Stec, W. J. *J. Chem. Soc., Perkin Trans. 1* **1987**, 1645.