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Palladium(II) Acetate Catalyzed Cyclization–Coupling of (*o*-Ethynylphenyl)phosphonic Acid Monoesters with Allyl Halides

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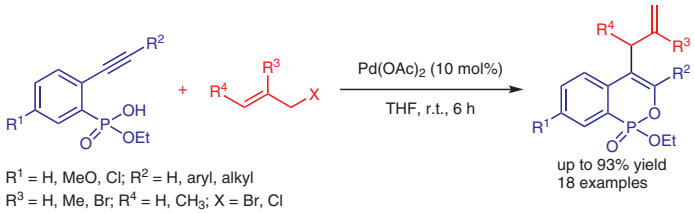

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Abstract A $Pd(OAc)_2$-catalyzed tandem cyclization–coupling reaction of (*o*-ethynylphenyl)phosphonic acid monoesters and allyl halides has been developed. This reaction provides an efficient, mild, general and regioselective way to synthesize 4-allylphosphaisocoumarins.

Key words cyclizations, coupling, tandem reactions, palladium(II) catalysis, phosphorus heterocycles, allylation

In our previous work, we synthesized a series of phosphaisocoumarins using CuI-catalyzed cyclization[1] and halocyclization[2] reactions, and identified them as a class of potent inhibitors of pancreatic cholesterol esterase (CEase).[3] We have also shown that 3,4-disubstituted phosphaisocoumarins could be obtained by a two-step process consisting of halocyclization of (*o*-ethynylphenyl)phosphonates followed by a cross-coupling reaction.[2] Due to their novel structure and potential biological activities, phosphaisocoumarins have attracted much attention among synthetic chemists. Lee[4] and Miura[5] independently demonstrated that Rh-catalyzed C–H bond activation of phosphonic acid monoesters with alkynes could be used to generate phosphaisocoumarins. Fañanás-Mastral[6] developed a copper-catalyzed tandem carboarylation/cyclization of alkynyl phosphonates with diaryliodonium salts for the synthesis of phosphaisocoumarins. Although these procedures are short and efficient, they have the disadvantages of having a narrow substrate range and often leading to regioisomeric mixtures when the resulting phosphaisocoumarins bear different substituents at positions 3 and 4. To further study the biological activity of this kind of phosphorus heterocycles, it is still highly desirable to develop more efficient, general, and applicable methods to prepare phosphaisocoumarins with various substituents.

The transition-metal-catalyzed cyclization–coupling reaction has received great research interest, since it can not only construct carbo- and heterocycles efficiently, but also introduce a new substituent in a one-pot process.[7] In the last decades, the tandem cyclization of carboxylic acids or esters,[8] amides,[9] phenols,[9e,10] and active methylene compounds[11] to alkynes, and coupling with aryl halides or alkenes has been extensively investigated and widely applied to the formation of highly functionalized oxygen- and nitrogen-containing heterocycles. Ma[12] has synthesized various allyl-substituted cyclic compounds via the palladium-catalyzed cyclization–coupling of functionalized allenes with allyl halides. However, this strategy has rarely been utilized to construct phosphorus-containing heterocycles.[13] Ding[13a] reported the preparation of 4-allylphosphaisocoumarins by CuI-catalyzed cyclization–coupling of (*o*-ethynylphenyl)phosphonic acid monoesters and allyl bromide. Unfortunately, Ding's method requires heating at 90 °C in DMF and was only suitable for coupling with allyl bromide. To overcome these limitations, we decided to reinvestigate the cyclization–coupling of (*o*-ethynylphenyl)phosphonic acid monoesters in the hope of providing a milder and more general way to synthesize 4-allyl-substituted phosphaisocoumarins.

We initiated this study with the reaction of (*o*-ethynylphenyl)phosphonic acid monoester **1a** (0.2 mmol) and allyl bromide (1.0 mmol). ^{31}P NMR spectroscopy and TLC were used to monitor the reaction process and the results are summarized in Table 1. When the reaction was catalyzed by $Pd(OAc)_2$ (10 mol%) in $CHCl_3$ at room temperature for 6 hours, the ^{31}P NMR yield of the target product **2a** was 90% (entry 1). Apart from **2a**, trace amounts of starting material **1a** and the direct cyclization product **3a** were detected. Under similar experimental conditions, $PdCl_2$ resulted in 81% ^{31}P NMR yield of **2a**, while $PdCl_2(PPh_3)_2$, $Pd(PPh_3)_4$, $AgNO_3$, and CuI gave no desired product **2a**, but a considerable

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amount of starting material **1a** and trace amounts of **3a** (entries 2–6). Further studies indicated that $Pd(OAc)_2$ (10 mol%) was necessary. When the amount of $Pd(OAc)_2$ was decreased to 5 mol% or 2 mol%, the yield of **2a** reduced (entry 1 vs entries 7 and 8). As also reported by Ding,[13a] we found that the presence of base has a negative effect on this reaction. When Et_3N was added (0.2 equiv or 1 equiv), the yield of **2a** dropped from 90% (no Et_3N used) to 87% and 48%, respectively, while the yield of **3a** increased from 5% (no Et_3N used) to 7% and 49%, respectively, indicating that the base promotes the production of byproduct **3a** (entry 1 vs entries 9 and 10). Screening solvents revealed that toluene gave **2a** in only 45% yield (entry 12) and MeCN gave **2a** in 58% yield (entry 14), whereas $CHCl_3$, DMF, and THF were all effective for this reaction (entries 1, 11, and 13). Taking into account that DMF is difficult to remove and THF gave cleaner results than $CHCl_3$, we chose THF as the solvent for the following reactions.

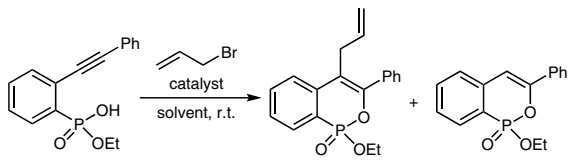
With these conditions in hand, the scope of this reaction was then explored; the results are summarized in Table 2. In the presence of $Pd(OAc)_2$ (10 mol%), the cyclization–coupling reaction of a series of (*o*-ethynylphenyl)phosphonic acid monoethyl esters **1** with allyl bromide proceeded smoothly in THF under open air at room temperature, leading to a variety of 4-allylphosphaisocoumarins **2a–n** in good to excellent yields within 6 hours (entries 1–14). The present reaction is quite versatile. Functionalities such as alkyl and aryl at the terminus of the alkynes, and chloro and methoxy on the benzene ring of compound **1** are all tolerated under the reaction conditions. The yields of the desired products **2** were partly affected by the nature of the substituents of **1**. For those cases where R^2 is an aryl group, the yields of **2** are generally excellent (entries 1–4, 7–9, 11–13). However, for those cases where R^2 is an alkyl group, such as cyclopropyl and *n*-butyl, the yields of **2** are only moderate (entries 5, 10, 14). This result is not surprising, since our previous studies have shown that these substrates with alkyl group at the terminus of alkynes are susceptible to self-cyclization to **3**, which is the main competitive reaction to the present cyclization–coupling reaction. Apart from internal alkynes, a terminal alkyne with R^2 = H (**1f**) also underwent the cyclization–coupling reaction, leading to the desired product **2f** in 59% yield (entry 6).

We then extended the reaction to other terminal allyl halides (Table 2, entries 15–19). Allyl halides where R^3 is a bromo or a methyl group worked well, giving the desired product **2o**, **2p**, and **2q** in 83–88% yield (entries 15–17). Further studies showed that allyl chloride gave even better results than allyl bromide did (entry 1 vs entry 18). When allyl chloride was used instead of allyl bromide, the yield of **2j** increased from 48% to 55% (entry 10 vs entry 19).

The reactions of **1a** with some γ-substituted allyl bromides were also examined (Scheme 1). Under the standard conditions, the reaction of **1a** with 1-bromobut-2-ene proceeded smoothly, affording two diastereomers **2rA** and **2rB** in 80% total yield; they contain one carbon chiral center and one phosphorus chiral center. At the same time, the isomers **2r′** (*E*/*Z*) and the direct cyclization product **3r** were detected in the ^1H and ^{31}P NMR spectra of the crude products. Unfortunately, after column chromatography of the reaction mixture, we only obtained pure **2rA** for full structural identification. We then tried to realize the cyclization–coupling of **1a** with allyl bromide bearing a phenyl group or two methyl groups at the γ position. However, all attempts to promote these two reactions, including prolonging the reaction time, raising the reaction temperature, and increasing the amount of the allyl bromide, resulted in failure. These results indicate that the reaction is affected by the steric hindrance of the C–C double bond.

Just like our previous cyclization reactions of phosphonates with alkynes,[1,2] the present reaction also shows high 6-*endo*-*dig* regioselectivity for six-membered-ring products, and no 5-*exo*-*dig* five-membered ring products were detected in either case. The structures of **2** were confirmed by spectroscopic methods, in particular by ^1H NMR spectral

Table 1 Optimization of the Bromocyclization of **1a**[a]

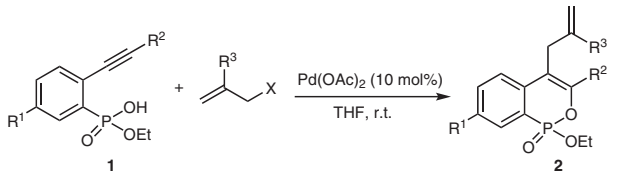


1a **2a** **3a**

Entry	Catalyst	Solvent	Ratio of **1a**/**2a**/**3a**[b]
1	$Pd(OAc)_2$	$CHCl_3$	5:90:5
2	$PdCl_2$	$CHCl_3$	6:81:13
3	$PdCl_2(PPh_3)_2$	$CHCl_3$	100:0:0
4[c]	$Pd(PPh_3)_4$	$CHCl_3$	100:0:0
5	$AgNO_3$	$CHCl_3$	96:0:4
6	CuI	$CHCl_3$	83:0:17
7[d]	$Pd(OAc)_2$	$CHCl_3$	17:78:5
8[e]	$Pd(OAc)_2$	$CHCl_3$	19:75:6
9[f]	$Pd(OAc)_2$	$CHCl_3$	7:86:7
10[g]	$Pd(OAc)_2$	$CHCl_3$	3:48:49
11	$Pd(OAc)_2$	DMF	13:87:0
12	$Pd(OAc)_2$	toluene	48:45:7
13	$Pd(OAc)_2$	THF	11:89:0
14	$Pd(OAc)_2$	MeCN	36:58:6

[a] Reaction conditions: **1a** (0.2 mmol), allyl bromide (1.0 mmol), catalyst (0.02 mmol), solvent (1.0 mL), in air, r.t., 6 h.
[b] Determined by ^{31}P NMR spectroscopy of the crude reaction mixtures.
[c] Under nitrogen atmosphere.
[d] $Pd(OAc)_2$ (5 mol%) was used.
[e] $Pd(OAc)_2$ (2 mol%) was used.
[f] Et_3N (0.2 equiv) was added.
[g] Et_3N (1 equiv) was added.

Table 2 Substrate Scope of the Cyclization–Coupling Reaction[a]

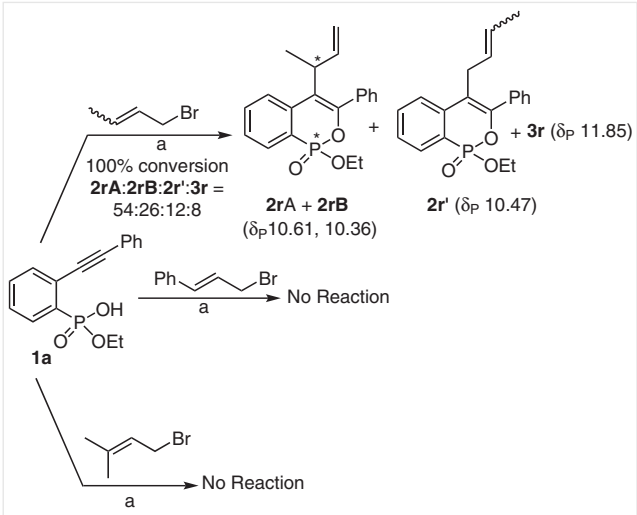


Entry	R^1	R^2	1	R^3	X	Product 2	Yield (%)[b]
1	H	Ph	**1a**	H	Br	**2a**	85
2	H	4-MeOC$_6$H$_4$	**1b**	H	Br	**2b**	82
3	H	4-MeC$_6$H$_4$	**1c**	H	Br	**2c**	63
4	H	4-FC$_6$H$_4$	**1d**	H	Br	**2d**	83
5	H	cyclopropyl	**1e**	H	Br	**2e**	58[c]
6	H	H	**1f**	H	Br	**2f**	59
7	OMe	Ph	**1g**	H	Br	**2g**	93
8	OMe	4-MeC$_6$H$_4$	**1h**	H	Br	**2h**	89
9	OMe	4-FC$_6$H$_4$	**1i**	H	Br	**2i**	76
10	OMe	cyclopropyl	**1j**	H	Br	**2j**	48[d]
11	Cl	Ph	**1k**	H	Br	**2k**	77
12	Cl	4-MeOC$_6$H$_4$	**1l**	H	Br	**2l**	59
13	Cl	4-FC$_6$H$_4$	**1m**	H	Br	**2m**	90
14	Cl	*n*-Bu	**1n**	H	Br	**2n**	48[e]
15	H	Ph	**1o**	Br	Br	**2o**	83
16	H	Ph	**1p**	Me	Br	**2p**	85
17	MeO	Ph	**1q**	Me	Br	**2q**	88
18	H	Ph	**1a**	H	Cl	**2a**	93
19	OMe	cyclopropyl	**1j**	H	Cl	**2j**	55[f]

[a] Reaction conditions: **1** (1.0 mmol), allyl halide (5.0 mmol), Pd(OAc)$_2$ (0.1 mmol), THF (5.0 mL), r.t., 6 h.
[b] Isolated yield.
[c] Side product **3e** (40%) was detected by ^{31}P NMR analysis of the crude mixtures.
[d] Side product **3j** (42%) was detected by ^{31}P NMR analysis of the crude mixtures.
[e] Side product **3n** (15%) was detected by ^{31}P NMR analysis of the crude mixtures.
[f] Side product **3j** (28%) was detected by ^{31}P NMR analysis of the crude mixtures.

analysis of the olefinic proton signals (see the experimental section and the supporting information). For example, compound **2f** has one olefinic proton at the 3-position resonating at δ = 6.60, with a coupling constant to phosphorus of 18.0 Hz, which is consistent with the six-membered ring structure and the literature.[13a]

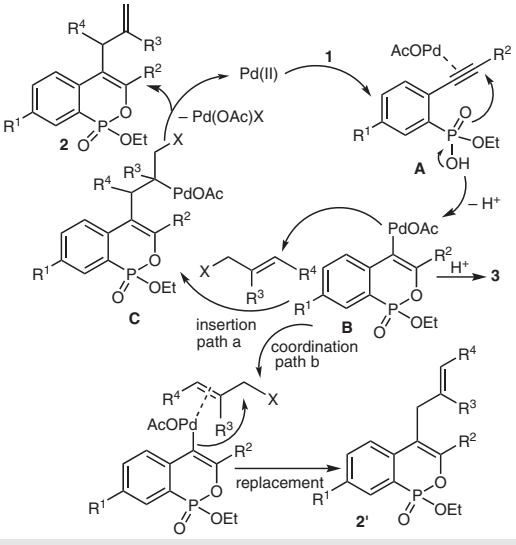
According to the above results and the related literature,[12,14] two possible mechanisms are proposed. Scheme 2 illustrates the Pd(II)-catalyzed pathway. The coordination of the alkynyl moiety of **1** to Pd(OAc)$_2$ activates the triple bond and forms the Pd complex **A**. Regioselective nucleophilic attack of the oxygen of the phosphonyl group to the activated



(a) reaction conditions: Pd(OAc)$_2$ (10 mol%), THF, r.t., 6 h

Scheme 1 The reaction of **1a** with γ-substituted allyl bromides

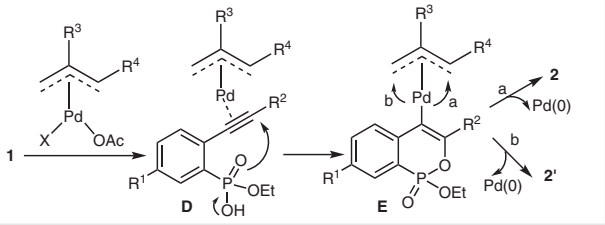
triple bond in an *endo* mode would give the vinylpalladium intermediate **B**, followed by insertion of the carbon–carbon bond of allylic halide to give a σ-carbonpalladium intermediate **C**, which undergoes β-elimination giving the desired product **2** with regeneration of the Pd(II) catalyst (path a). On the other hand, the vinylpalladium intermediate **B** may coordinate with the C–C double bond of the allyl halide and then directly replace the halide to give **2′** (path b).[12b] At the same time, intermediate **B** could also undergo protonation and lead to the direct cyclization product **3**, which is competitive with the target product. Scheme 3 shows the Pd(0)-catalyzed pathway, which involves the coordination of the π-allylpalladium species with the triple bond of **1** to form



Scheme 2 Proposed Pd(II)-catalyzed pathway

intermediate **D**, followed by cyclocarbopalladation to give vinylpalladium(II) **E**, and, finally, reductive elimination of **E**, to give **2** or **2′** and regenerate Pd(0).

We speculate that the reaction might be more likely to proceed via the Pd(II)-catalyzed mechanism than the Pd(0)-catalyzed mechanism, on the basis of the following facts. First of all, $Pd(PPh_3)_4$, which is expected to be more reactive than Pd(II) catalysts in the Pd(0)-catalyzed mechanism, could not catalyze the present reaction at all (Table 1, entry 4). Besides, if the current reaction proceeds via the Pd(0)-catalyzed pathway, the reaction of **1a** with 1-bromobut-2-ene should produce a higher or comparable yield of **2r′** compared to **2r**, due to smaller steric hindrance in path b than in path a (Scheme 3). However, we obtained the contrary result, in which the yield of **2r** is much higher than that of **2r′** (Scheme 1).



Scheme 3 Proposed Pd(0)-catalyzed pathway

In conclusion, we demonstrated that 4-allylphosphaisocoumarins could be prepared by a $Pd(OAc)_2$-catalyzed cyclization–coupling reaction of (*o*-ethynylphenyl)phosphonic acid monoesters and allylic halides under mild conditions. Compared with Ding's procedure[13a] to synthesize 4-allylphosphaisocoumarins, which requires heating at 90 °C in DMF, the advantages of the present method include that the reaction can be carried out in THF at room temperature, has a wider substrate scope, and can couple with various substituted allyl halides.

The ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Varian INOVA 400 NMR instrument. All melting points are uncorrected. HRMS was carried out using an Agilent Technologies 6230 TOF LC/MS mass spectrometer. IR spectra were recorded using KBr pellets on a Bruker Equinox 55 FT/IR spectrophotometer. Column chromatography was performed on 200–300 mesh silica gel. Thin-layer chromatography was conducted on Kieselgel 60 F254. The products **–2b–e,h–j,l–r** are new compounds; their structures are identified by their ^1H, ^{13}C, and ^{31}P NMR, HRMS, and IR data. Compounds **2a,f,g,k** are known compounds; their identities are confirmed by ^1H, ^{13}C, and ^{31}P NMR spectra which are consistent with the related literature.[13a] Starting materials **1** were readily prepared from the basic hydrolysis of the corresponding phosphonic acid diethyl esters, which were synthesized by the Pd-catalyzed cross-coupling reaction of the corresponding phenyl perfluoroalkanesulfonates with alkynes according to our previous procedures.[1,15]

Benzo[*c*][1,2]oxaphosphinine 1-Oxides 2 by $Pd(OAc)_2$-Catalyzed Coupling–Cyclization of (*o*-Ethynylphenyl)phosphonic Acid Monoesters 1 with Allylic Halides; General Procedure

Allyl bromide (5 mmol) was added dropwise at r.t. to a mixture of compound **1** (1 mmol) and $Pd(OAc)_2$ (0.1 mmol) in THF (5 mL). After stirring at r.t. under open air for 6 h, the reaction mixture was evaporated in vacuo and the residue was purified by column chromatography (silica gel, PE/EtOAc, 10:1 to 1:1); this gave the corresponding product **2**.

4-Allyl-1-ethoxy-3-phenylbenzo[*c*][1,2]oxaphosphinine 1-Oxide (2a)

Yield: 277 mg (85%); white solid; mp 79.2–80 °C.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.94–7.89 (m, 1 H), 7.62–7.52 (m, 4 H), 7.47–7.41 (m, 4 H), 6.09–5.99 (m, 1 H), 5.20–5.08 (m, 2 H), 4.28–4.18 (m, 2 H), 3.43–3.29 (m, 2 H), 1.32 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 149.25 (d, *J* = 10.4 Hz), 138.84 (d, *J* = 6.9 Hz), 136.21, 134.73 (d, *J* = 5.6 Hz), 133.05 (d, *J* = 2.4 Hz), 129.56, 129.47, 128.58, 128.29, 127.60 (d, *J* = 15.6 Hz), 125.71 (d, *J* = 12.4 Hz), 121.69 (d, *J* = 180.1 Hz), 117.11, 113.42 (d, *J* = 11.7 Hz), 63.04 (d, *J* = 6.5 Hz), 32.77, 16.56 (d, *J* = 6.2 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 10.77.

4-Allyl-1-ethoxy-3-(4-methoxyphenyl)benzo[*c*][1,2]oxaphosphinine 1-Oxide (2b)

Yield: 292 mg (82%); white solid; mp 120.7–120.9 °C.

IR (KBr): 2984, 1628, 1605, 1508, 1473, 1438, 1244, 1174, 1082, 1024 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.92–7.8 (m, 1 H), 7.61–7.57 (m, 1 H), 7.54–7.48 (m, 3 H), 7.43–7.39 (m, 1 H), 6.92 (d, *J* = 9.2 Hz, 2 H), 6.09–5.99 (m, 1 H), 5.18–5.06 (m, 2 H), 4.24–4.17 (m, 2 H), 3.84 (s, 3 H), 3.43–3.29 (m, 2 H), 1.30 (t, *J* = 7.1 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 160.44, 149.22 (d, *J* = 10.3 Hz), 139.12 (d, *J* = 7.1 Hz), 136.39, 133.00 (d, *J* = 2.5 Hz), 130.07, 129.45 (d, *J* = 8.9 Hz), 127.34 (d, *J* = 15.6 Hz), 127.14 (d, *J* = 5.8 Hz), 125.65 (d, *J* = 12.4 Hz), 121.56 (d, *J* = 179.8 Hz), 117.07, 113.63, 112.59 (d, *J* = 11.4 Hz), 62.98 (d, *J* = 6.5 Hz), 55.45, 32.97, 16.57 (d, *J* = 6.1 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 10.94.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{20}H_{21}NaO_4P$: 379.1070; found: 379.1075.

4-Allyl-1-ethoxy-3-(*p*-tolyl)benzo[*c*][1,2]oxaphosphinine 1-Oxide (2c)

Yield: 214 mg (63%); light yellow solid; mp 95–96 °C.

IR (KBr): 2981, 1628, 1509, 1474, 1439, 1269, 1243, 1026 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.91 (dd, *J* = 14.7, 7.3 Hz, 1 H), 7.63–7.59 (m, 1 H), 7.54–7.41 (m, 4 H), 7.21 (d, *J* = 7.6 Hz, 2 H), 6.08–5.99 (m, 1 H), 5.18 (d, *J* = 9.2 Hz, 1 H), 5.10 (d, *J* =17.6 Hz, 1 H), 4.25–4.18 (m, 2 H), 3.40–3.29 (m, 2 H), 2.39 (s, 3 H), 1.31 (t, *J* = 7.1 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 149.33 (d, *J* = 10.4 Hz), 139.46, 138.90 (d, *J* = 7.0 Hz), 136.22, 132.91 (d, *J* = 2.5 Hz), 131.79 (d, *J* = 5.7 Hz), 129.39 (d, *J* = 8.9 Hz), 128.86, 128.40 (s), 127.35 (d, *J* = 15.5 Hz), 125.56 (d, *J* = 12.4 Hz), 121.53 (d, *J* = 179.8 Hz), 116.95, 112.94 (d, *J* = 11.6 Hz), 62.88 (d, *J* = 6.5 Hz), 32.75, 21.41, 16.46 (d, *J* = 6.1 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 10.82.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{20}H_{21}NaO_3P$: 363.1121; found: 363.1121.

4-Allyl-1-ethoxy-3-(4-fluorophenyl)benzo[*c*][1,2]oxaphosphinine 1-Oxide (2d)

Yield: 286 mg (83%); light yellow solid; mp 116–116.8 °C.

IR (KBr): 2924, 1629, 1595, 1507, 1476, 1440, 1268, 1240, 1157, 1026 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.91 (dd, *J* = 14.8, 7.5 Hz, 1 H), 7.65–7.53 (m, 4 H), 7.48–7.43 (m, 1 H), 7.13–7.08 (t, *J* =8.7 Hz, 2 H), 6.09–6.00 (m, 1 H), 5.21–5.18 (m, 1 H), 5.11–5.07 (m, 1 H), 4.26–4.19 (m, 2 H), 3.38–3.28 (m, 2 H), 1.32 (t, *J* = 7.1 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 164.40, 161.92, 148.20, 138.54, 135.97, 132.99 (d, *J* = 2.5 Hz), 130.51 (d, *J* = 8.4 Hz), 129.41 (d, *J* = 8.9 Hz), 127.60 (d, *J* = 15.6 Hz), 125.63 (d, *J* = 12.4 Hz), 121.60 (d, *J* = 180.1 Hz), 117.14, 115.29 (d, *J* = 21.8 Hz), 113.39 (d, *J* = 11.4 Hz), 63.02 (d, *J* = 6.5 Hz), 32.71, 16.47 (d, *J* = 6.1 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 10.81.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{19}H_{18}FNaO_3P$: 367.0870; found: 367.0876.

4-Allyl-3-cyclopropyl-1-ethoxybenzo[*c*][1,2]oxaphosphinine 1-Oxide (2e)

Yield: 168 mg (58%); yellow oil.

IR (KBr): 2983, 1648, 1596, 1559, 1475, 1443, 1263, 1163, 1019 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.78 (dd, *J* = 14.9, 7.5 Hz, 1 H), 7.55–7.51 (m, 1 H), 7.36–7.28 (m, 2 H), 6.00–5.91 (m, 1 H), 5.10–5.05 (m, 2 H), 4.16–4.04 (m, 2 H), 3.45–3.30 (m, 2 H), 1.88–1.81 (m, 1 H), 1.27 (t, *J* = 7.6 Hz, 3 H), 1.15–1.08 (m, 1 H), 0.97–0.91 (m, 1 H), 0.84–0.77 (m, 2 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 151.11 (d, *J* = 9.9 Hz), 139.34 (d, *J* = 7.0 Hz), 134.85, 133.00 (d, *J* = 2.4 Hz), 129.30 (d, *J* = 9.3 Hz), 126.29 (d, *J* = 15.8 Hz), 123.83 (d, *J* = 12.3 Hz), 120.60 (d, *J* = 180.9 Hz), 116.00, 110.50 (d, *J* = 12.0 Hz), 62.65 (d, *J* = 6.5 Hz), 31.21, 16.39 (d, *J* = 6.1 Hz), 11.78 (d, *J* = 5.4 Hz), 6.30, 5.40.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 11.62.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{16}H_{19}NaO_3P$: 313.0964; found: 313.0966.

4-Allyl-1-ethoxybenzo[*c*][1,2]oxaphosphinine 1-Oxide (2f)

Yield: 148 mg (59%); yellow oil.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.87 (dd, *J* = 14.7, 7.5 Hz, 1 H), 7.60 (t, *J* = 7.7 Hz, 1 H), 7.43–7.38 (m, 2 H), 6.66 (d, *J* = 18.0 Hz, 1 H), 5.95–5.85 (m, 1 H), 5.17–5.08 (m, 2 H), 4.23–4.11 (m, 2 H), 3.25–3.12 (m, 2 H), 1.31 (t, *J* = 7.0 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 139.32 (d, *J* = 10.4 Hz), 137.49 (d, *J* = 6.6 Hz), 135.18, 133.15 (d, *J* = 2.4 Hz), 130.04 (d, *J* = 8.8 Hz), 128.04 (d, *J* = 15.6 Hz), 124.51 (d, *J* = 11.6 Hz), 121.72 (d, *J* = 179.7 Hz), 117.54, 117.12 (d, *J* = 13.9 Hz), 77.26 (s), 63.16 (d, *J* = 6.6 Hz), 32.74, 16.50 (d, *J* = 6.1 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 11.25.

4-Allyl-1-ethoxy-7-methoxy-3-phenylbenzo[*c*][1,2]oxaphosphinine 1-Oxide (2g)

Yield: 331 mg (93%); yellow oil.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.58–7.56 (m, 2 H), 7.48–7.44 (m, 1 H), 7.42–7.37 (m, 4 H), 7.15 (dd, *J* = 8.9, 2.8 Hz, 1 H), 6.06–5.98 (m, 1 H), 5.19–5.07 (m, 2 H), 4.26–4.17 (m, 2 H), 3.89 (s, 3 H), 3.38–3.29 (m, 2 H), 1.32 (t, *J* = 7.1 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 158.79 (d, *J* = 19.1 Hz), 147.40 (d, *J* = 10.4 Hz), 136.33, 134.80 (d, *J* = 5.8 Hz), 131.66 (d, *J* = 6.3 Hz), 129.27, 128.59, 128.27, 127.65 (d, *J* = 14.7 Hz), 122.95 (d, *J* = 179.1 Hz), 120.34 (d, *J* = 2.9 Hz), 117.08, 113.26 (d, *J* = 11.4 Hz), 112.70 (d, *J* = 10.2 Hz), 63.01 (d, *J* = 6.5 Hz), 55.81, 32.86, 16.59 (d, *J* = 6.3 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 10.77.

4-Allyl-1-ethoxy-7-methoxy-3-(*p*-tolyl)benzo[*c*][1,2]oxaphosphinine 1-Oxide (2h)

Yield: 330 mg (89%); yellow oil.

IR (KBr): 2976, 1604, 1557, 1491, 1251, 1229, 1024 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.47–7.36 (m, 4 H), 7.22–7.13 (m, 3 H), 6.06–5.99 (m, 1 H), 5.18–5.06 (m, 2 H), 4.24–4.16 (m, 2 H), 3.88 (s, 3 H), 3.38–3.28 (m, 2 H), 2.39 (s, 3 H), 1.31 (t, *J* = 7.1 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 158.68 (d, *J* = 18.9 Hz), 147.56 (d, *J* = 10.5 Hz), 139.31, 136.41, 131.93 (d, *J* = 5.8 Hz), 131.83 (d, *J* = 6.5 Hz), 128.95, 128.48, 127.58 (d, *J* = 14.7 Hz), 122.85 (d, *J* = 179.0 Hz), 120.32 (d, *J* = 2.8 Hz), 117.01, 112.86 (d, *J* = 11.4 Hz), 112.64 (d, *J* = 10.2 Hz), 62.95 (d, *J* = 6.5 Hz), 55.79, 32.93, 21.50, 16.58 (d, *J* = 6.1 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 10.81.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{21}H_{23}NaO_4P$: 393.1226; found: 393.1232.

4-Allyl-1-ethoxy-3-(4-fluorophenyl)-7-methoxybenzo[*c*][1,2]oxaphosphinine 1-Oxide (2i)

Yield: 285 mg (76%); yellow oil.

IR (KBr): 2979, 1604, 1557, 1507, 1492, 1441, 1252, 1226, 1160, 1023 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.56–7.52 (m, 2 H), 7.47–7.35 (m, 2 H), 7.14 (dd, *J* = 8.9, 2.8 Hz, 1 H), 7.09–7.05 (m, 2 H), 6.06–5.97 (m, 1 H), 5.18–5.04 (m, 2 H), 4.24–4.16 (m, 2 H), 3.86 (s, 3 H), 3.36–3.21 (m, 2 H), 1.30 (t, *J* = 7.1 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 164.31, 161.83, 158.79 (d, *J* = 19.1 Hz), 146.29 (d, *J* = 10.4 Hz), 136.09, 131.37 (d, *J* = 6.4 Hz), 130.49 (d, *J* = 8.4 Hz), 127.62 (d, *J* = 14.7 Hz), 122.82 (d, *J* = 179.0 Hz), 120.24 (d, *J* = 2.8 Hz), 117.13, 115.29 (d, *J* = 21.7 Hz), 113.28 (d, *J* = 11.3 Hz), 112.70 (d, *J* = 10.2 Hz), 63.05 (d, *J* = 6.5 Hz), 55.72, 32.80, 16.52 (d, *J* = 6.1 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 10.78.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{20}H_{20}FNaO_4P$: 397.0975; found: 397.0971.

4-Allyl-3-cyclopropyl-1-ethoxy-7-methoxybenzo[*c*][1,2]oxaphosphinine 1-Oxide (2j)

Yield: 154 mg (48%); yellow oil.

IR (KBr): 2977, 1628, 1604, 1557, 1492, 1239, 1163, 1021 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.34–7.27 (m, 2 H), 7.10 (dd, *J* = 8.9, 2.7 Hz, 1 H), 6.01–5.92 (m, 1 H), 5.12–5.07 (m, 2 H), 4.16–4.07 (m, 2 H), 3.84 (s, 3 H), 3.44–3.31 (m, 2 H), 1.87–1.82 (m, 1 H), 1.30 (t, *J* = 7.1 Hz, 3 H), 1.13–1.09 (m, 1 H), 0.95–0.89 (m, 1 H), 0.84–0.75 (m, 2 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 157.95 (d, *J* = 19.3 Hz), 149.14 (d, *J* = 10.1 Hz), 135.14, 132.45 (d, *J* = 6.4 Hz), 125.86 (d, *J* = 14.7 Hz), 121.86 (d, *J* = 180.1 Hz), 120.48 (d, *J* = 2.8 Hz), 116.11, 112.57 (d, *J* = 10.6 Hz), 110.42 (d, *J* = 11.9 Hz), 62.77 (d, *J* = 6.5 Hz), 55.74, 31.43, 16.54 (d, *J* = 6.2 Hz), 11.68 (d, *J* = 5.5 Hz), 6.21, 5.28.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 11.61.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{17}H_{21}NaO_4P$: 343.1070; found: 343.1072.

4-Allyl-7-chloro-1-ethoxy-3-phenylbenzo[*c*][1,2]oxaphosphinine 1-Oxide (2k)

Yield: 277 mg (77%); yellow solid; mp 88.4–88.5 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86 (dd, *J* = 15.3, 2.3 Hz, 1 H), 7.57–7.54 (m, 3 H), 7.48–7.40 (m, 4 H), 6.05–5.96 (m, 1 H), 5.20–5.05 (m, 2 H), 4.28–4.21 (m, 2 H), 3.36–3.28 (m, 2 H), 1.33 (t, *J* = 7.1 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 149.47 (d, *J* = 10.4 Hz), 137.16 (d, *J* = 6.4 Hz), 135.85, 134.33 (d, *J* = 5.7 Hz), 133.47 (d, *J* = 20.9 Hz), 133.11 (d, *J* = 2.6 Hz), 129.64, 129.16 (d, *J* = 9.8 Hz), 128.50 (d, *J* = 4.3 Hz), 128.34 (d, *J* = 4.2 Hz), 127.45 (d, *J* = 13.6 Hz), 123.55 (d, *J* = 179.8 Hz), 117.30, 112.88 (d, *J* = 11.4 Hz), 63.38 (d, *J* = 6.5 Hz), 32.73, 16.55 (d, *J* = 6.1 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 8.72.

4-Allyl-7-chloro-1-ethoxy-3-(4-methoxyphenyl)benzo[*c*][1,2]oxaphosphinine 1-Oxide (2l)

Yield: 231 mg (59%); yellow solid; mp 97.6–98.2 °C.

IR (KBr): 2975, 2925, 1620, 1513, 1479, 1440, 1255, 1178, 1040, 1019 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85 (dd, *J* = 15.3, 2.2 Hz, 1 H), 7.56–7.51 (m, 3 H), 7.46–7.42 (m, 1 H), 6.93 (d, *J* = 8.8 Hz, 2 H), 6.08–5.99 (m, 1 H), 5.20 (d, *J* = 10.4 Hz, 1 H), 5.08 (d, *J* = 18.5 Hz, 1 H), 4.28–4.21 (m, 2 H), 3.85 (s, 3 H), 3.38–3.30 (m, 2 H), 1.34 (t, *J* = 7.1 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 160.61, 149.51 (d, *J* = 10.4 Hz), 137.51 (d, *J* = 6.5 Hz), 136.08, 133.36, 133.11 (d, *J* = 2.7 Hz), 130.06, 129.16 (d, *J* = 9.8 Hz), 127.41 (d, *J* = 13.6 Hz), 126.77 (d, *J* = 5.8 Hz), 123.44 (d, *J* = 179.5 Hz), 117.31, 113.71, 112.04 (d, *J* = 11.2 Hz), 63.38 (d, *J* = 6.5 Hz), 55.48, 33.00, 16.61 (d, *J* = 6.0 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 8.87.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{20}H_{20}ClNaO_4P$: 413.0680; found: 413.0681.

4-Allyl-7-chloro-1-ethoxy-3-(4-fluorophenyl)benzo[*c*][1,2]oxaphosphinine 1-Oxide (2m)

Yield: 341 mg (90%); yellow solid; mp 86.2–86.9 °C.

IR (KBr): 2925, 1604, 1508, 1472, 1392, 1262, 1235, 1158, 1105, 1028 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86 (dd, *J* = 15.3, 2.3 Hz, 1 H), 7.56–7.53 (m, 3 H), 7.47–7.43 (m, 1 H), 7.12–7.08 (m, 2 H), 6.07–5.98 (m, 1 H), 5.22–5.05 (m, 2 H), 4.29–4.22 (m, 2 H), 3.36–3.25 (m, 2 H), 1.35 (t, *J* = 7.1 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 164.62, 162.14, 148.51 (d, *J* = 10.3 Hz), 137.05 (d, *J* = 6.4 Hz), 135.76, 133.67 (d, *J* = 20.8 Hz), 133.22 (d, *J* = 2.6 Hz), 130.59 (d, *J* = 8.5 Hz), 129.24 (d, *J* = 9.8 Hz), 127.51 (d, *J* = 13.6 Hz), 123.58 (d, *J* = 179.9 Hz), 117.49, 115.50 (d, *J* = 21.8 Hz), 112.98 (d, *J* = 11.4 Hz), 63.55 (d, *J* = 6.5 Hz), 32.84, 16.62 (d, *J* = 6.0 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 8.76.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{19}H_{17}ClFNaO_3P$: 379.0661; found: 379.0665.

4-Allyl-3-butyl-7-chloro-1-ethoxybenzo[*c*][1,2]oxaphosphinine 1-Oxide (2n)

Yield: 170 mg (48%); yellow oil.

IR (KBr): 2961, 2930, 2872, 1631, 1474, 1264, 1158, 1027 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78 (dd, *J* = 15.3, 2.0 Hz, 1 H), 7.49 (dd, *J* = 8.8, 2.0 Hz, 1 H), 7.32–7.28 (m, 1 H), 5.94–5.85 (m, 1 H), 5.09–4.99 (m, 2 H), 4.23– 4.17 (m, 2 H), 3.29–3.19 (m, 2 H), 2.45–2.35 (m, 2 H), 1.66–1.58 (m, 2 H), 1.41–1.37 (m, 2 H), 1.32 (t, *J* = 7.1 Hz, 3 H), 0.94 (t, *J* = 7.3 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 152.70 (d, *J* = 11.0 Hz), 137.38 (d, *J* = 6.3 Hz), 134.75, 133.05 (d, *J* = 2.5 Hz), 132.72 (d, *J* = 20.9 Hz), 129.13 (d, *J* = 9.9 Hz), 126.27 (d, *J* = 13.4 Hz), 122.98 (d, *J* = 179.8 Hz), 116.47, 110.89 (d, *J* = 11.9 Hz), 63.08 (d, *J* = 6.5 Hz), 31.90 (d, *J* = 5.1 Hz), 31.66, 29.15, 22.39, 16.52 (d, *J* = 6.2 Hz), 13.97.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 8.92.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{17}H_{22}ClNaO_3P$: 363.0887; found: 363.0891.

4-(2-Bromoallyl)-1-ethoxy-3-phenylbenzo[*c*][1,2]oxaphosphinine 1-Oxide (2o)

Yield: 336 mg (83%); white solid; mp 106.6–106.9 °C.

IR (KBr): 2983, 1619, 1474, 1431, 1272, 1242, 1072, 1017 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93 (dd, *J* = 14.5, 7.3 Hz, 1 H), 7.68–7.64 (m, 1 H), 7.59–7.57 (m, 2 H), 7.49–7.44 (m, 5 H), 5.65 (d, *J* = 2.0 Hz, 1 H), 5.61 (d, *J* = 2.0 Hz, 1 H), 4.28–4.21 (m, 2 H), 3.77–3.65 (m, 2 H), 1.32 (t, *J* = 7.1 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 150.50 (d, *J* = 10.3 Hz), 137.88 (d, *J* = 6.8 Hz), 134.08 (d, *J* = 5.6 Hz), 133.27 (d, *J* = 2.5 Hz), 131.07, 129.82, 129.56 (d, *J* = 8.9 Hz), 128.46, 128.17, 127.90 (d, *J* = 15.7 Hz), 125.18 (d, *J* = 12.3 Hz), 121.47 (d, *J* = 180.6 Hz), 118.47, 112.75 (d, *J* = 11.7 Hz), 63.08 (d, *J* = 6.5 Hz), 41.52, 16.50 (d, *J* = 6.1 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 10.54.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{19}BrO_3P$: 405.0250; found:405.0255.

1-Ethoxy-4-(2-methylallyl)-3-phenylbenzo[*c*][1,2]oxaphosphinine 1-Oxide (2p)

Yield: 289 mg (85%); white solid; mp 83.6–84.1 °C.

IR (KBr): 2975, 1598, 1476, 1444, 1274, 1243, 1156, 1121, 1075, 1022 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91 (dd, *J* = 14.8, 7.9 Hz, 1 H), 7.63–7.57 (m, 3 H), 7.46–7.39 (m, 5 H), 4.93 (s, 1 H), 4.75 (s, 1 H), 4.27–4.17 (m, 2 H), 3.29–3.17 (m, 2 H), 1.81 (s, 3 H), 1.32 (t, *J* = 7.1 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 149.11 (d, *J* = 10.3 Hz), 143.59, 139.04 (d, *J* = 7.0 Hz), 134.67 (d, *J* = 5.7 Hz), 132.92 (d, *J* = 2.4 Hz), 129.32 (d, *J* = 4.3 Hz), 129.21, 128.24 (d, *J* = 13.3 Hz), 127.54, 127.38, 125.66 (d, *J* = 12.4 Hz), 121.51 (d, *J* = 180.0 Hz), 113.70 (d, *J* = 11.6 Hz), 112.4, 62.89 (d, *J* = 6.4 Hz), 37.09, 23.24, 16.47 (d, *J* = 6.3 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 10.96.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{22}O_3P$: 341.1301; found: 341.1302.

1-Ethoxy-7-methoxy-4-(2-methylallyl)-3-phenylbenzo[c][1,2]oxaphos-phinine 1-oxide (2q)

Yield: 326 mg (88%); yellow oil.

IR (KBr): 2980, 1608, 1454, 1260, 1242, 1228, 1156, 1121, 1075, 1022 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59–7.56 (m, 2 H), 7.42–7.34 (m, 5 H), 7.14 (dd, *J* = 8.9, 2.8 Hz, 1 H), 4.92 (s, 1 H), 4.74 (s, 1 H), 4.26–4.19 (m, 2 H), 3.88 (s, 3 H), 3.27–3.15 (m, 2 H), 1.80 (s, 3 H), 1.32 (t, *J* = 7.0 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 158.76 (d, *J* = 19.1 Hz), 147.39 (d, *J* = 10.6 Hz), 143.77, 134.85 (d, *J* = 5.8 Hz), 131.97 (d, *J* = 6.4 Hz), 129.22, 128.33 (d, *J* = 15.4 Hz), 127.67 (d, *J* = 14.8 Hz), 122.87 (d, *J* = 179.1 Hz), 120.34 (d, *J* = 2.8 Hz), 113.64 (d, *J* = 11.4 Hz), 112.54, 112.43, 100.12, 62.95 (d, *J* = 6.5 Hz), 55.79, 37.27, 23.31, 16.59 (d, *J* = 6.2 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 10.90.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{24}O_4P$: 371.1407; found: 371.1403.

4-(But-3-en-2-yl)-1-ethoxy-3-phenylbenzo[*c*][1,2]oxaphosphinine 1-Oxide (2rA)

Yield: 170 mg (50%); yellow oil.

IR (KBr): 2922, 2852, 1596, 1471, 1262, 1082, 1020 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94 (dd, *J* = 14.8, 7.6 Hz, 1 H), 7.84–7.76 (m, 1 H), 7.59–7.52 (m, 3 H), 7.46–7.38 (m, 4 H), 6.24–6.16 (m, 1 H), 5.26–5.17 (m, 2 H), 4.24 (dd, *J* = 15.0, 7.5 Hz, 2 H), 3.73–3.71 (m, 1 H), 1.38–1.29 (m, 6 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 149.09 (d, *J* = 10.4 Hz), 142.79, 137.77 (d, *J* = 6.6 Hz), 135.09 (d, *J* = 5.4 Hz), 132.31 (d, *J* = 2.3 Hz), 130.01 (d, *J* = 9.3 Hz), 129.67, 128.97, 128.54, 127.85 (d, *J* = 12.1 Hz), 127.48 (d, *J* = 15.6 Hz), 122.97 (d, *J* = 179.9 Hz), 119.24 (d, *J* = 11.5 Hz), 115.33, 62.89 (d, *J* = 6.2 Hz), 37.72, 18.43, 16.75 (d, *J* = 6.2 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 10.77.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{22}O_3P$: 341.1301; found: 341.1300.

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Supporting Information

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