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Ruthenium-Catalyzed C−H Activation/Cyclization for the Synthesis of Phosphaisocoumarins

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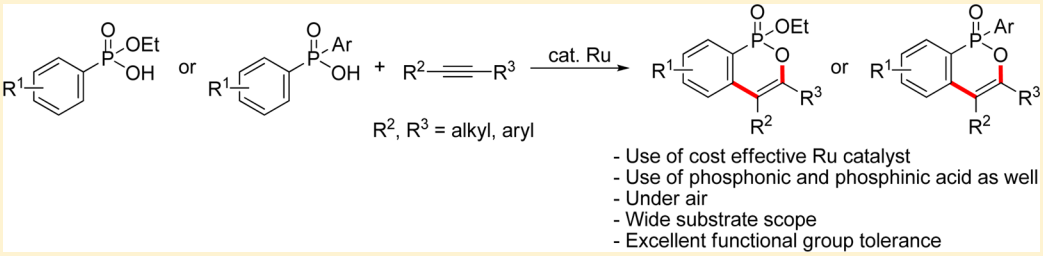
Supporting Information

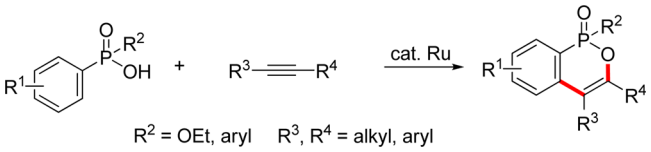


ABSTRACT: An efficient and cost-effective ruthenium-catalyzed oxidative cyclization of phosphonic acid monoesters or phosphinic acids with alkynes has been developed for the synthesis of a wide range of phosphaisocoumarins in good to excellent yields under aerobic conditions. A multitude of arylphosphonic acid monoesters and arylphosphinic acids having electron-donating and -withdrawing groups were oxidatively cyclized. Various diarylacetylenes, dialkylacetylenes, and alkylarylacetylenes effectively underwent the ruthenium-catalyzed oxidative cyclization. A substrate possessing benzoic acid as well as a phenylphosphonic monoester moiety was smoothly cyclized with hex-3-yne to afford a compound having both isocoumarin and phosphaisocoumarin moieties. Alkenylphosphonic monoester afforded phosphorus 2-pyrone through oxidative cyclization with alkyne. Competition experiments between diaryl- and dialkylalkynes and between diarylacetylenes having *p*-methoxy and *p*-chloro groups gave results which showed that the present oxidative cyclizations were not affected by the electronic effects of alkynes. Mechanistic studies revealed C−H bond metalation to be the rate-limiting step.

INTRODUCTION

Because heterocyclic compounds are ubiquitous in nature, the development of new methods for their preparation is very important.[1] In addition, phosphorus compounds are an essential component due to their significant biological and pharmaceutical properties.[2] Hence, Kim's group and ours have recently been interested in the development of new phosphoryl-related directing groups in C−H bond activation and its application to the synthesis of phosphorus heterocyclic compounds.[3] To date, phosphorus heterocycles have been generally prepared by Pd-catalyzed intramolecuar cyclizations of alkynes derived from prefunctionalized phosphorus compounds having an *o*-halo-substituted aryl moiety.[4] During the past decade, transition-metal-catalyzed C−H activation[5] without prefunctionalization has been recognized as an important tool for atom- and step-economical syntheses of heterocyclic compounds.[6] Recently, rhodium- and ruthenium-catalyzed oxidative cyclizations of alkynes by carboxylic acids have been reported by Miura,[7] Ackermann,[8] and Jeganmohan,[9] respectively. In addition, synthetic methods of phosphaisocoumarins were demonstrated through rhodium-catalyzed cyclization using alkynes and organophosphorus compounds.[3c,10] Herein, we report the cost-effective ruthenium-catalyzed C−H activation/cyclization of phosphonic monoesters and phosphinic acids for the synthesis of phosphaisocoumarins (Scheme 1).

Scheme 1. Ru-Catalyzed Cyclization using Phosphonic and Phosphinic Acids



RESULTS AND DISCUSSION

We commenced our investigations by examining the C−H activation/cyclization of ethyl phenylphosphonic monoester (**1a**) using a variety of oxidants and solvents in the presence of $[RuCl_2(p\text{-cymene})]_2$ (2 mol %) and KPF_6 (20 mol %) in *t*-BuOH (Table 1). When $Cu(OAc)_2{\cdot}H_2O$, $Na_2S_2O_8$, and $PhI(OAc)_2$ were used as oxidants, the cyclization did not proceed (entries 1−3). However, the use of Ag_2CO_3 and AgOAc promoted the cyclization, thus producing the phosphaisocoumarin **3a** in 14% and 32% yields, respectively. Further screening of oxidant revealed that the addition of Ag_2CO_3/AgOAc (1 equiv each) as a co-oxidant improved the yield up to 36% (entry 6). Solvent screening (*t*-AmOH, DCE, and PhCl) failed to increase the yield (entries 7−9). Because phosphaisocoumarin **3a** was

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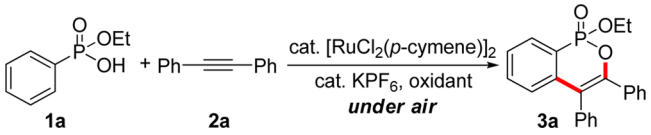
Table 1. Reaction Optimization[a]



entry	oxidant (amt (equiv))	solvent	temp (°C)	time (h)	yield[b] (%)
1	$Cu(OAc)_2·H_2O$ (1)	*t*-BuOH	120	20	0
2	$Na_2S_2O_8$ (1)	*t*-BuOH	120	20	0
3	$PhI(OAc)_2$ (1)	*t*-BuOH	120	20	0
4	Ag_2CO_3 (1)	*t*-BuOH	120	20	14 (76)
5	AgOAc (1)	*t*-BuOH	120	20	32 (65)
6	Ag_2CO_3 (1)/AgOAc (1)	*t*-BuOH	120	20	36 (56)
7	Ag_2CO_3 (1)/AgOAc (1)	*t*-AmOH	120	20	20 (60)
8	Ag_2CO_3 (1)/AgOAc (1)	DCE	120	20	17
9	Ag_2CO_3 (1)/AgOAc (1)	PhCl	120	20	0
10	Ag_2CO_3 (1)/AgOAc (1)	*t*-BuOH	90	16	39 (55)
11[c]	Ag_2CO_3 (1)/AgOAc (1)	*t*-BuOH	90	16	45 (46)
12[d]	Ag_2CO_3 (1)/AgOAc (1)	*t*-BuOH	90	16	93 (85,[f] 5)
13[d]	Ag_2CO_3 (1)/AgOAc (1)	*t*-BuOH	90	30	97 (91[f])
14[d,e]	Ag_2CO_3 (1)/AgOAc (1)	*t*-BuOH	90	16	63

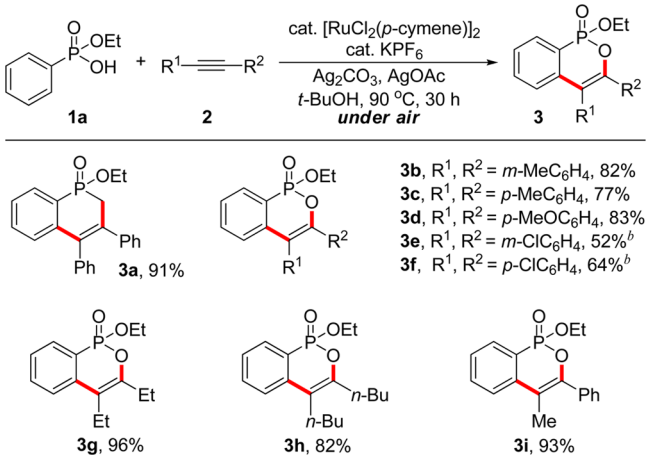
[a]Conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), $[RuCl_2(p\text{-cymene})]_2$ (2 mol %), KPF_6 (20 mol %). [b]Yields based on ^1H NMR integration relative to CH_2Br_2 internal standard. Numbers in parentheses are recovery yields of **1a**. [c]$[RuCl_2(p\text{-cymene})]_2$ (6 mol %) was used. [d]$[RuCl_2(p\text{-cymene})]_2$ (10 mol %) was used. [e]KPF_6 was not used. [f]Isolated yield.

unstable at 120 °C, the cyclization was conducted at 90 °C, thus providing **3a** in 39% yield for 16 h (entry 10). When 6 and 10 mol % of $[RuCl_2(p\text{-cymene})]_2$ were used, the desired product **3a** was obtained in 45% and 93% yields, respectively, along with **1a** at 90 °C for 16 h (entries 11 and 12). Optimal results were obtained with Ag_2CO_3/AgOAc (1 equiv each) in the presence of $[RuCl_2(p\text{-cymene})]_2$ (10 mol %) and KPF_6 (20 mol %) in *t*-BuOH (90 °C, 30 h) to afford **3a** in 91% isolated yield under aerobic conditions (entry 13). The reaction gave **3a** in 63% yield in the absence of KPF_6, indicating that the use of KPF_6 is essential for a excellent yield (entry 14).[8]

First, we examined the scope and limitation of the Ru-catalyzed C−H activation/cyclization with a variety of internal alkynes **2** under the optimized reaction conditions (Scheme 2). Subjecting **1a** to diverse electron-rich diaryl-substituted alkynes produced the desired phosphaisocoumarins **3b−d** in good to excellent yields under aerobic conditions. However, electron-deficient diaryl-substituted alkynes having a chloro group were less reactive and the corresponding phosphaisocoumarins **3e,f** were isolated in 52% and 64% yields, respectively, in the presence of 15 mol % of Ru catalyst. Dialkyl-substituted alkynes such as hex-3-yne and dec-5-yne were cyclized with high yields, providing the desired phosphaisocoumarins **3g,h**. The unsymmetrical disubstituted alkyne could be used to establish unique reactivity, thereby demonstrating the effectiveness of the developed reaction. 1-Phenyl-1-propyne afforded the desired product **3i** (93%) selectively.

Encouraged by these results, we investigated the scope of arylphosphonic monoesters **1** having useful functional groups with diphenylethyne and hex-3-yne (Scheme 3). Cyclization of substrate **1b** bearing an electron-donating *o*-methoxy group produced the phosphaisocoumarins **3j,k** in 76% and 74% yields, respectively, under aerobic conditions. In the case of **1c**, with an *m*-methoxy group, C−H bond activation occurred

Scheme 2. Scope of Alkynes Reacting with Phosphonic Acid[a]



[a]Conditions: **1a** (0.2 mmol), **2** (0.3 mmol), $[RuCl_2(p\text{-cymene})]_2$ (10 mol %), KPF_6 (20 mol %), Ag_2CO_3 (0.2 mmol), AgOAc (0.2 mmol), *t*-BuOH (1.3 mL). [b]$[RuCl_2(p\text{-cymene})]_2$ (15 mol %) was used.

simultaneously at C2 as well as at C6 to afford **3l** (55%) and **3m** (33%). Formation of **3m** in spite of steric hindrance might be explained by cooperative coordination of both the methoxy and the phosphonic acid groups.[3c] Substrates with a halogen atom furnished the desired compounds in high yields. Indeed, the *p*-fluoro-substituted substrate **1e** was reacted with diphenylethyne and hex-3-yne, affording the phosphaisocoumarins **3o,p**. Arylphosphonic monoesters possessing chloro (**1f**), bromo (**1g**), and ketone (**1h**) groups were smoothly cyclized to give **3q−t** in high yields. The tolerance of chloro, bromo, and ketone groups is especially significant, as successive functional group transformations are hopeful. Substrates **1i,j** possessing 2,3-dimethyl and 2-methyl-4-methoxy groups at the phenyl ring, respectively, worked equally well. In contrast, in the case of 3,4-(methylenedioxy)phenylphosphonic monoester **1k**, C−H activation took place at C2 instead of C6 to give rise to **3y** in 81% yield because coordination of both the 3-oxy and the phosphonic acid group likely triggers functionalization at the C2 site. Ethyl naphthalen-1-ylphosphonic monoester **1l** gave the cyclic compound **3z** in 82% yield.

Next, reactions of diphenylphosphinic acid **4a** with a multitude of alkynes **2** were screened (Scheme 4). C−H activated cyclization of **4a** proceeded smoothly with diaryl-substituted alkynes under aerobic conditions. Exposure of **4a** to diphenylethyne produced phosphaisocoumarin **5a** in quantitative yield (98%). When alkynes **2** having a *m*-methyl, *p*-methyl, or *p*-methoxy group at the phenyl ring were cyclized with **4a**, the phosphaisocoumarins **5b−d** were obtained in good to excellent yields. Electron-deficient bis(chlorophenyl)ethyne also produced **5e,f**. We were pleased to obtain phosphaisocoumarins **5g,h**, albeit in moderate yields, from **4a** and bis(bromophenyl)ethyne. The tolerance of chloro and bromo groups at the phenyl ring is especially useful, providing an opportunity for further functionalization. In addition, diphenylphosphinic acid **4a** was reacted with hex-3-yne or dec-5-yne smoothly, thus producing the desired phosphaisocoumarins **5i,j** in 82% and 74% yields, respectively.

When substrate **4b**, bearing an *o*-methyl group, was cyclized with diphenylethyne and hex-3-yne, **5k,l** were produced in 76% and 74% yields, respectively (Scheme 5). The effectiveness of the present reaction was proved by direct cyclization of electron-rich and -deficient substrates **4c,d**. Phosphinic acid **4e**,

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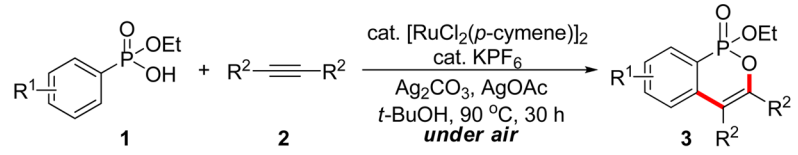
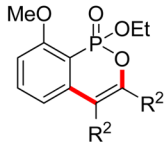
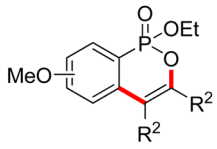
Scheme 3. Scope of Phosphonic Acids and Alkynes[a]



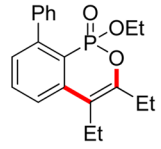
R^1 = *o*-MeO (**1b**), *m*-MeO (**1c**), *o*-Ph (**1d**), *p*-F (**1e**), *o*-Cl (**1f**), *m*-Br (**1g**), *p*-Ac (**1h**) 2,3-$(Me)_2$ (**1i**), 2-Me-4-MeO (**1j**), 3,4-(OCH_2O) (**1k**), R^1-C_6H_4 = naphthalen-1-yl (**1l**)



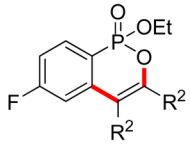
3j, R^2 = Ph, 76%
3k, R^2 = Et, 74%



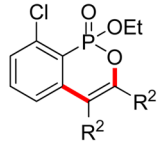
3l (7-MeO), R^2 = Et, 55%
3m (5-MeO), R^2 = Et, 33%



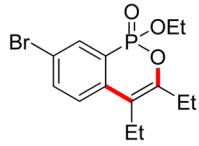
3n, 70%[a]



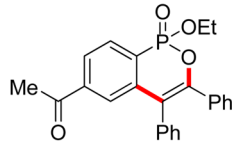
3o, R^2 = Ph, 73%
3p, R^2 = Et, 77%



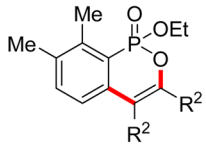
3q, R^2 = Ph, 81%
3r, R^2 = Et, 85%



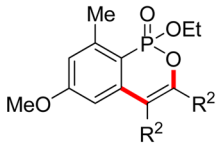
3s, 74%[a]



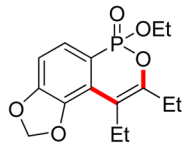
3t, 71%



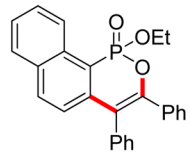
3u, R^2 = Ph, 97%
3v, R^2 = Et, 97%



3w, R^2 = Ph, 75%
3x, R^2 = Et, 93%



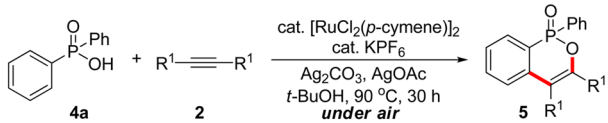
3y, 81%

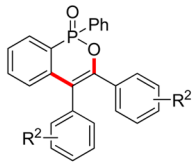


3z, 82%

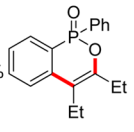
[a]$[RuCl_2(p\text{-cymene})]_2$ (15 mol %) was used.

Scheme 4. Scope of Alkynes Reacting with Phosphinic Acid[a]

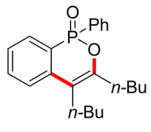




R^2 = H, **5a**, 98%
R^2 = *m*-Me, **5b**, 60%
R^2 = *p*-Me, **5c**, 72%
R^2 = *p*-MeO, **5d**, 95%
R^2 = *m*-Cl, **5e**, 60%
R^2 = *p*-Cl, **5f**, 83%
R^2 = *m*-Br, **5g**, 45%
R^2 = *p*-Br, **5h**, 56%

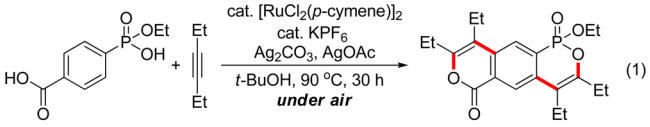


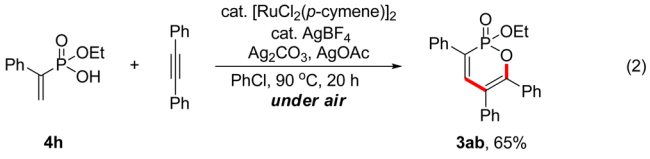
5i, 82%



5j, 74%

[a]$[RuCl_2(p\text{-cymene})]_2$ (15 mol %) was used.





having a naphthalen-1-yl group, worked as well, resulting in the formation of **5q** in 80% yield. Gratifyingly, we obtained the single product **5r** (70%) from mesityl(phenyl)phosphinic acid **4f** and hex-3-yne.

Moreover, compound **4g**, possessing benzoic acid as well as a phenylphosphonic monoester moiety, was smoothly cyclized with hex-3-yne to afford **3aa** in 91% yield under the optimum reaction conditions (eq 1). We were pleased to obtain the phosphorus 2-pyrone **3ab** from the reaction of ethyl (1-phenylvinyl)-phosphonic monoester **4h** with diphenylethyne under the modified reaction conditions (see the Supporting Information and eq 2).

Competition experiments between alkynes were examined (Scheme 6). Phenylphosphonic monoester **1a** was treated with diphenylethyne and hex-5-yne (1.5 equiv each) to give the phosphaisocoumarins **3a** (42%) and **3g** (42%) (eq 3). A competition experiment between diarylacetylenes having *p*-methoxy and *p*-chloro groups afforded the phosphaisocoumarins **3d** (27%) and **3f** (31%) (eq 4). These results indicate that cyclization of phosphonic acid monoesters is not affected by the electronic effects of alkynes.

Next, we conducted kinetic isotope effect (KIE) studies to obtain insight into the reaction mechanism (Scheme 7). A significant

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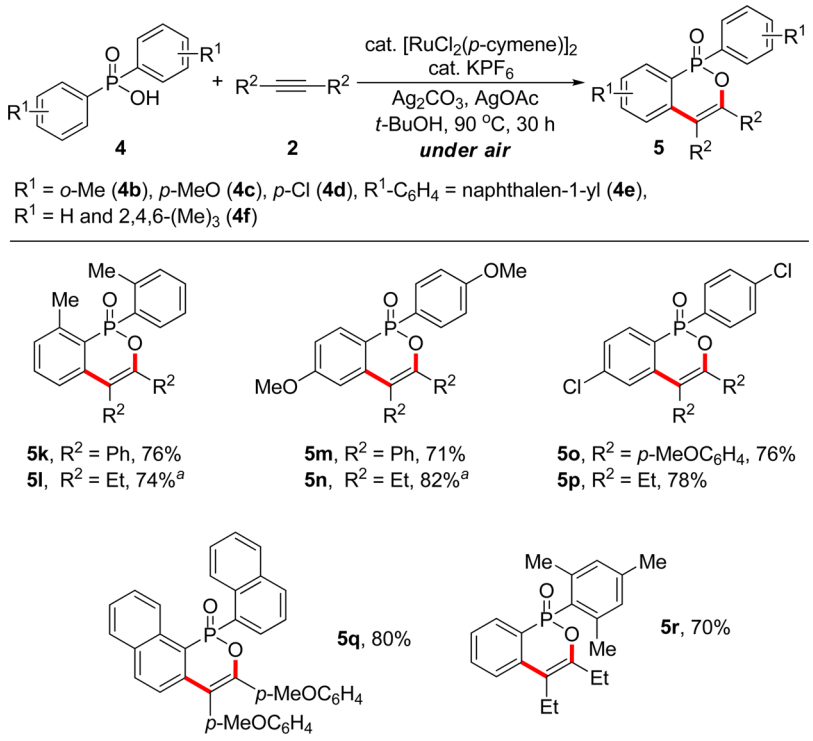
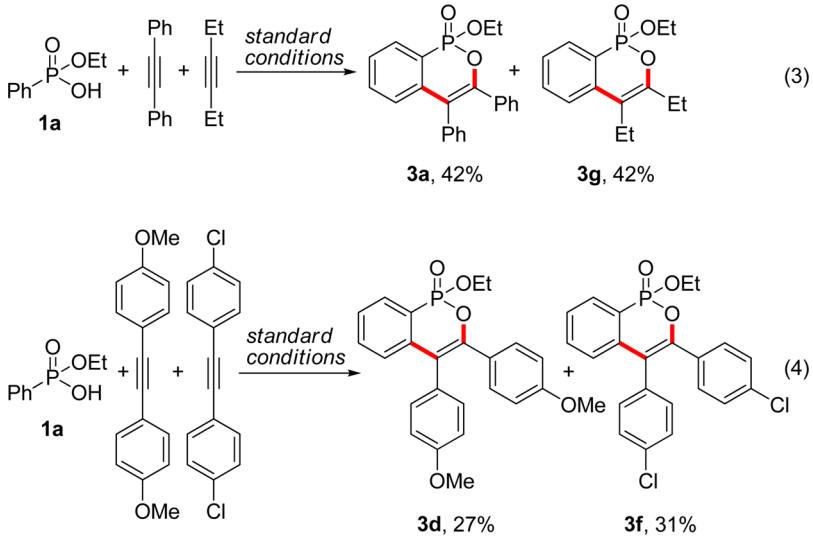
Scheme 5. Scope of Phosphinic Acids with Alkynes[a]



[a][RuCl2(p-cymene)]2 (15 mol %) was used.

Scheme 6. Intermolecular Competition Experiments



KIE was detected (k_H/k_D = 5.16), suggesting that C−H bond cleavage at the 2-position of the phosphonic monoester is most probably associated with the rate-limiting step. We also conducted kinetic isotope effect (KIE) studies of diphenylphosphinic acid. An obvious KIE was observed (k_H/k_D = 5.67), indicating that the C−H bond cleavage at the 2-position of phosphinic acid is most likely involved with the rate-limiting step.

A plausible mechanism for the reaction of phosphonic and phosphinic acids **1** and **4** with alkynes **2** is described in Scheme 8. A proposed catalytic cycle began by coordination of **1** and **4** to $RuLCl_2$ to afford the ruthenium(III) phosphonate **I**. Successive ortho ruthenation to give the ruthenacycle intermediate **II**, alkyne insertion, and reductive elimination occurred to produce the phosphaisocoumarins **3** and **5**.

CONCLUSION

In summary, we have developed an efficient and cost-effective ruthenium-catalyzed oxidative cyclization of phosphonic acid monoesters or phosphinic acids with alkynes for the synthesis of a wide range of phosphaisocoumarins in good to excellent yields under aerobic conditions. A variety of arylphosphonic acid monoesters and arylphosphinic acids having electron-donating and -withdrawing groups were oxidatively cyclized. A number of diarylacetylenes, dialkylacetylenes, and alkylarylacetylenes effectively underwent the ruthenium-catalyzed oxidative

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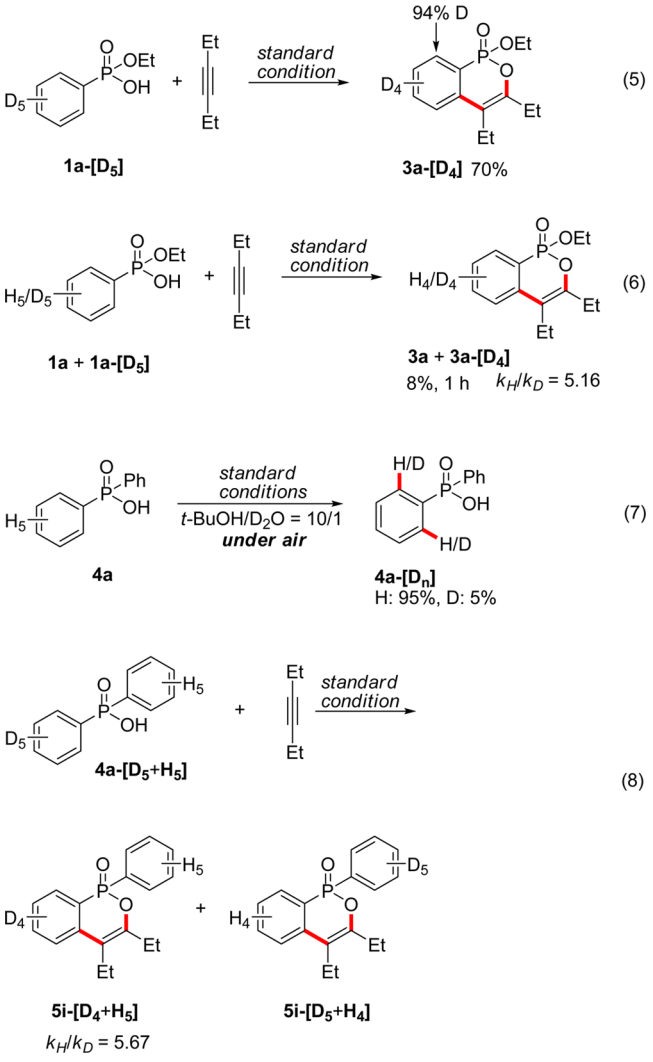
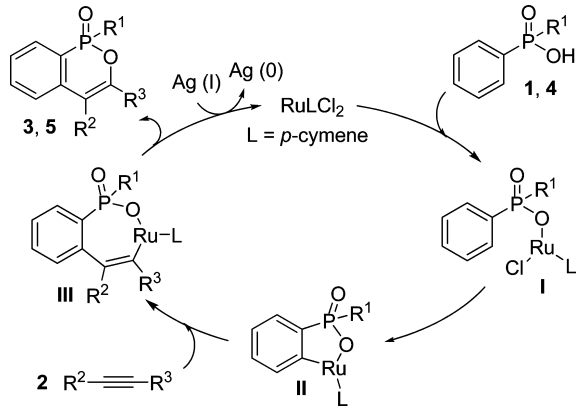
Scheme 7. Studies with Isotopically Labeled Compounds



Scheme 8. Plausible Mechanism



cyclization. A substrate possessing benzoic acid as well as a phenylphosphonic monoester moiety was smoothly cyclized with hex-3-yne to afford a compound having both isocoumarin and phosphaisocoumarin moieties. An alkenylphosphonic monoester provided phosphorus 2-pyrone through oxidative cyclization with alkyne. Competition experiments between diaryl- and dialkylalkynes and between diarylacetylenes having *p*-methoxy and *p*-chloro groups gave the results that the present oxidative cyclizations were not affected by the electronic effects of alkynes. Mechanistic studies revealed the C−H bond metalation to be the rate-limiting step.

EXPERIMENTAL SECTION

General Procedure for the Ru-Catalyzed Oxidative Cyclization of Arylphosphonic Monoester 1 with Alkynes 2. In a screw-top V-vial were added phenyl phosphonic monoester (**1a**; 37.0 mg, 0.2 mmol), diphenylethyne (**2a**; 53.0 mg, 0.3 mmol), $[RuCl_2(p\text{-cymene})]_2$ (12.3 mg, 0.02 mmol), KPF_6 (7.0 mg, 0.04 mmol), Ag_2CO_3 (55.0 mg, 0.2 mmol), and AgOAc (33.0 mg, 0.2 mmol) in *t*-BuOH (1.3 mL). The resulting mixture was stirred in air at 90 °C (bath temperature) for 30 h. After Celite filtration and evaporation of the solvents in vacuo, the crude product was purified by column chromatography on silica gel (EtOAc/hexane 1/3) to yield **3a** (66.0 mg, 91%) as a white solid.

*3,4-Diphenyl-1-ethoxybenz[c-1,2]oxaphosphinine 1-oxide (**3a**):* R_f = 0.3 (EtOAc/hexane 1/3); white solid, mp 123−126 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94−7.92 (m, 1H), 7.50−7.40 (m, 2H), 7.39−7.33 (m, 3H), 7.25−7.11 (m, 7H), 6.98−6.93 (m, 1H), 4.33−4.19 (m, 2H), 1.32 (t, J = 7.08 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8 (d, J = 10.66 Hz), 140.2 (d, J = 6.95 Hz), 136.0, 134.5 (d, J = 5.85), 132.8 (d, J = 3.50 Hz), 131.5, 129.3 (d, J = 9.11 Hz), 128.89, 128.85, 128.5, 127.8, 127.66, 127.64 (d, J = 15.33 Hz), 127.1 (d, J = 11.91 Hz), 120.9 (d, J = 181.70 Hz), 119.8 (d, J = 12.02 Hz), 63.0 (d, J = 7.21 Hz), 16.4 (d, J = 5.86 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ 10.58; IR (film) 2982, 1591, 1469, 1443, 1275, 1023, 953, 757 cm^{-1}; HRMS (EI) m/z calcd for $C_{22}H_{19}O_3P$ 362.1072, found 362.1072.

Procedure for Rh-Catalyzed Oxidative Cyclization of Ethyl Phenylvinylphosphonic Monoester 4h with Diphenylethyne. In a screw-top V-vial were added ethyl phenylvinylphosphonic monoester (**4h**; 42.4 mg, 0.2 mmol), diphenylethyne (**2a**; 53.0 mg, 0.3 mmol), $[RuCl_2(p\text{-cymene})]_2$ (12.3 mg, 0.02 mmol), KPF_6 (7.0 mg, 0.04 mmol), Ag_2CO_3 (55.0 mg, 0.2 mmol), and AgOAc (33.0 mg, 0.2 mmol) in PhCl (1.3 mL). The resulting mixture was stirred under air at 90 °C (bath temperature) for 20 h. After Celite filtration and evaporation of the solvents in vacuo, the crude product was purified by column chromatography on silica gel (EtOAc/hexane 1/1) to yield **3ab** (50.5 mg, 65%) as a colorless oil.

*2-Ethoxy-3,5,6-triphenyl-1,2-oxaphosphorin 2-oxide (**3ab**):* R_f = 0.3 (EtOAc/hexane 1/1); colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72−7.70 (m, 2H), 7.42−7.34 (m, 3H), 7.31−727 (m, 5H), 7.25−7.17 (m, 6H), 4.28−4.18 (m, 2H), 1.29 (t, J = 7.08 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.8 (d, J = 12.76 Hz), 142.1, 142.0, 138.1 (d, J = 1.18 Hz), 134.7 (d, J = 10.11 Hz), 133.2 (d, J = 6.04 Hz), 129.5, 129.3, 129.1, 128.9 (d, J = 4.51 Hz), 128.5, 127.8, 127.6, 127.1 (d, J = 7.30 Hz), 124.2 (d, J = 168.42 Hz), 117.7 (d, J = 16.17 Hz), 63.7 (d, J = 6.99 Hz), 16.3 (d, J = 6.06 Hz); ^{31}P NMR (161 MHz, $CDCl_3$) δ 9.49; IR (film) 2982, 2240, 1615, 1536, 1444, 1260, 1159, 1036, 968, 756 cm^{-1}; HRMS (EI) m/z calcd for $C_{24}H_{21}O_3P$ 388.1228, found 388.1227.

General Procedure for the Ru-Catalyzed Oxidative Cyclization of Diarylphosphinic Acid 4 with Alkynes 2. In a screw-top V-vial were added diphenylphosphinic acid (**4a**; 43.6 mg, 0.2 mmol), diphenylethyne (**2a**; 53.0 mg, 0.3 mmol), $[RuCl_2(p\text{-cymene})]_2$ (12.3 mg, 0.02 mmol), KPF_6 (7.0 mg, 0.04 mmol), Ag_2CO_3 (55.0 mg, 0.2 mmol), and AgOAc (33.0 mg, 0.2 mmol) in *t*-BuOH (1.3 mL). The resulting mixture was stirred in air at 90 °C (bath temperature) for 30 h. After Celite filtration and evaporation of the solvents in vacuo, the crude product was purified by column chromatography on silica gel (EtOAc/hexane 1/2) to yield **5a** (77.3 mg, 98%) as a solid.

*1,3,4-Triphenyl-1H-2,1-benzoxaphosphorin-1-oxide (**5a**):* R_f = 0.5 (EtOAc/hexane 1/1); pale yellow solid, mp 140−142 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98−7.92 (m, 2H), 7.64−7.57 (m, 2H), 7.55−7.50 (m, 2H), 7.45 (tt, J = 7.8, 1.3 Hz, 1H), 7.41−7.30 (m, 4H), 7.29−7.27 (m, 2H), 7.24 (t, J = 1.6 Hz, 1H), 7.23 (t, J = 2.0 Hz, 1H), 7.18−7.08 (m, 3H), 7.05 (dd, J = 7.9, 4.8, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.9 (d, J = 11.1 Hz) 138.7 (d, J = 5.3 Hz), 136.1, 134.7 (d, J = 5.2 Hz), 133.0 (d, J = 2.8 Hz), 132.5 (d, J = 2.5 Hz), 132.4 (d, J = 11.1 Hz),

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131.6, 130.3 (d, J = 12.4 Hz), 130.1 (d, J = 145.2 Hz), 129.1, 128.9, 128.6, 128.5 (d, J = 3.4 Hz), 127.9, 127.7, 127.5, 126.8 (d, J = 9.5 Hz), 123.2 (d, J = 128.7 Hz), 119.1 (d, J = 11.1 Hz); ^{31}P NMR (161 MHz, $CDCl_3$) δ 24.43; IR (film) 3056, 1590, 1240, 1122, 950, 736 cm^{-1}; HRMS (EI) m/z calcd for $C_{26}H_{19}O_2P$ 394.1123, found 394.1123.

Experiments with Isotopically Labeled Substrates. A solution of 2,3,4,5,6-pentadeuteriophenylphosphonic monoester (**1a**-[$\mathbf{D_5}$]) (38.0 mg, 0.2 mmol), hex-3-yne (**2g**; 35.0 μL, 0.3 mmol), [$RuCl_2$(*p*-cymene)]$_2$ (12.3 mg, 0.02 mmol), KPF_6 (7.0 mg, 0.04 mmol), Ag_2CO_3 (55.0 mg, 0.2 mmol), and AgOAc (33 mg, 0.2 mmol) in *t*-BuOH (1.3 mL) was stirred in air at 90 °C (bath temperature) for 30 h. After Celite filtration and evaporation of the solvents in vacuo, the crude product was purified by column chromatography on silica gel (EtOAc/hexane 1/3) to yield (**3a**-[$\mathbf{D_4}$]) (38.0 mg, 70%) as a colorless oil.

A mixture of phenylphosphonic monoester (**1a**; 18 mg, 0.1 mmol), 2,3,4,5,6-pentadeuteriophenyl phosphonic monoester (**1a**-[$\mathbf{D_5}$]; 19.0 mg, 0.1 mmol), hex-3-yne (**2g**; 35.0 μL, 0.3 mmol), [$RuCl_2$(p-cymene)]$_2$ (12.3 mg, 10 mol %), Ag_2CO_3 (55.0 mg, 0.2 mmol), and AgOAc (33.0 mg, 0.2 mmol) in *t*-BuOH (1.3 mL) was stirred in air at 90 °C (bath temperature) for 1 h. After Celite filtration and evaporation of the solvents in vacuo, the crude product was purified by column chromatography on silica gel (EtOAc/hexane 1/3) to yield **3a** + **3a**-[$\mathbf{D_4}$] (4.0 mg, 8%) as a colorless oil.

In a screw-top V-vial were added diphenylphosphinic acid (**4a**; 43.6 mg, 0.2 mmol), [$RuCl_2$(*p*-cymene)]$_2$ (12.3 mg, 0.02 mmol), KPF_6 (7.0 mg, 0.04 mmol), Ag_2CO_3 (55.0 mg, 0.2 mmol), and AgOAc (33.0 mg, 0.2 mmol) in *t*-BuOH (1.3 mL) and D_2O (0.13 mL). The resulting mixture was stirred in air at 90 °C (bath temperature) for 30 h. After Celite filtration and evaporation of the solvents in vacuo, the crude product was purified by column chromatography on silica gel (EtOAc/hexane 1/2) to yield (39.3 mg, 90%, **4a** + **4a**-[$\mathbf{D_n}$]) as a solid.

In a screw-top V-vial were added phenyl(2′, 3′, 4′, 5′, 6′-pentadeuteriophenyl)phosphinic acid (**4a**-[$\mathbf{D_5}$+$\mathbf{H_5}$]; 44.6 mg, 0.2 mmol), hex-3-yne (35.0 μL, 0.3 mmol), [$RuCl_2$(*p*-cymene)]$_2$ (12.3 mg, 0.02 mmol), KPF_6 (7.0 mg, 0.04 mmol), Ag_2CO_3 (55.0 mg, 0.2 mmol), and AgOAc (33.0 mg, 0.2 mmol) in *t*-BuOH (1.3 mL). The resulting mixture was stirred in air at 90 °C (bath temperature) for 2 h. After Celite filtration and evaporation of the solvents in vacuo, the crude product was purified by column chromatography on silica gel (EtOAc/hexane 1/2) to yield **5i**-[$\mathbf{D_4}$+$\mathbf{H_5}$] + **5i**-[$\mathbf{D_5}$+$\mathbf{H_4}$] (8.0 mg, 13%) as a oil.

Preparation of Phosphonic Monoesters 1 and 4.[3c] The corresponding diethyl phosphonate (1.0 mmol), NaOH (2.0 mmol), and H_2O (5.0 mL) were stirred at 80 °C for 6−12 h. The reaction solution was diluted with water (10 mL). The solution was neutralized with cooled concentrated hydrochloric acid and extracted with EtOAc. The extracts were evaporated under reduced pressure to give **1a**−**k** and **4b**−**h**, which were used as such in the next reaction.

*Phenylphosphonic acid monoethyl ester (**1a**):* colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.12 (s, 1H), 7.83−7.77 (m, 2H), 7.54−7.50 (m, 1H), 7.44−7.37 (m, 2H), 4.09−4.02 (m, 2H), 1.28 (t, J = 7.06 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.1 (d, J = 2.95 Hz), 131.3 (d, J = 10.15 Hz), 128.9 (d, J = 194.07 Hz), 128.3 (q, J = 15.34 Hz), 61.9 (d, J = 5.81 Hz), 16.1 (d, J = 6.81 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ 20.36; IR (film) 2983, 2601, 1669, 1439, 1208, 1134, 1041, 990, 749 cm^{-1}; HRMS (EI) m/z calcd for $C_8H_{11}O_3P$ 186.0446, found 186.0448.

*(2-Methoxyphenyl)phosphonic acid monoethyl ester (**1b**):* colorless solid, mp 95−100 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.49 (s, 1H), 7.82 (ddd, J = 15.2, 7.5, 1.7 Hz, 1H), 7.49 (t, J = 7.5 Hz, 1H), 6.98 (td, J = 11.3, 3.0, 1H), 6.93 (dd, J = 7.7, 7.5 Hz, 1H) 4.18−4.11 (m, 2H), 3.87 (s, 3H), 1.33 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4 (d, J = 2.6 Hz), 134.4 (d, J = 7.1 Hz), 134.2, 120.3 (d, J = 14.9 Hz), 117.1 (d, J = 194.0 Hz), 111.2 (d, J = 9.5 Hz), 62.1 (d, J = 5.9 Hz), 55.9, 16.3 (d, J = 6.7 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ 20.02; IR (film) 2981, 2265, 1576, 1462, 1432, 1045, 987, 732 cm^{-1}; HRMS (EI) m/z calcd for $C_9H_{13}O_4P$ 216.0551, found 216.0551.

*(3-Methoxyphenyl)phosphonic acid monoethyl ester (**1c**):* colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.18 (s, 1H), 7.42−7.29 (m, 3H), 7.08−7.05 (m, 1H), 4.12−4.05 (m, 2H), 3.82 (s, 3H), 1.31 (t, J = 7.06 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4 (d, J = 19.19 Hz), 129.91 (d, J = 193.16 Hz), 129.67 (d, J = 18.15 Hz), 123.61 (d, J = 9.65 Hz), 118.79 (d, J = 3.11 Hz), 115.76 (d, J = 11.68 Hz), 62.12 (d, J = 5.81 Hz), 55.38; IR (film) 2983, 1579, 1424, 1241, 1036, 961 cm^{-1}; HRMS (EI) m/z calcd for $C_9H_{13}O_4P$ 216.0551, found 216.0550.

*(2-Biphenyl)phosphonic acid monoethyl ester (**1d**):* white solid, mp 107−114 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.84 (s, 1H), 8.04 (ddd, J = 14.8, 7.7, 0.7 Hz, 1H), 7.56 (t, J = 7.6 Hz, 1H), 7.45−7.40 (m, 3H), 7.38−7.31 (m, 4H), 3.75 (q, J = 7.2 Hz, 2H), 0.98 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.1 (d, J = 10.0 Hz), 141.3 (d, J = 4.3 Hz), 133.4 (d, J = 10.0 Hz), 132.0 (d, J = 2.8 Hz), 131.3 (d, J = 14.3 Hz), 129.4, 127.5, 127.4, 127.0 (d, J = 192.9 Hz), 126.8 (d, J = 15.0 Hz), 61.6 (d, J = 6. Four Hz), 15.7 (d, J = 7.2 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ 21.24; IR (film) 2981, 2286, 1468, 1392, 1096, 1039, 957, 778 cm^{-1}; HRMS (EI) m/z calcd for $C_{14}H_{15}O_3P$ 262.0759, found 262.0761.

*(4-Fluorophenyl)phosphonic acid monoethyl ester (**1e**):* pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.28 (s, 1H), 7.83−7.76 (m, 2H), 7.10 (dt, J = 13.03 Hz, 3.39 Hz, 2H), 4.09−4.02 (m, 2H), 1.29 (t, J = 7.06 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5 (d, J = 3.80 Hz), 164.0 (d, J = 3.77 Hz), 133.9 (q, J = 6.83 Hz), 115.6 (q, J = 12.71 Hz), 62.1 (d, J = 5.72 Hz), 16.1 (d, J = 6.68 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ 19.30; IR (film) 2985, 2262, 1594, 1504, 1226, 1132, 994, 834, 776 cm^{-1}; HRMS (EI) m/z calcd for $C_8H_{10}FO_3P$ 204.0352, found 204.0349.

*(2-Chlorophenyl)phosphonic acid monoethyl ester (**1f**):* yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.96 (s, 1H), 7.95 (dd, J = 13.7, 7.4 Hz, 1H), 7.48−7.42 (m, 2H), 7.34−7.29 (m, 1H), 4.21−4.13 (m, 2H), 1.36 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.9 (d, J = 3.5 Hz), 134.9 (d, J = 7.8 Hz), 133.5 (d, J = 2.3 Hz), 130.7 (d, J = 10.5 Hz), 127.8 (d, J = 199.1 Hz), 126.3 (d, J = 14.0 Hz), 62.6 (d, J = 6.0 Hz), 16.2 (d, J = 6.9 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ 16.66; IR (film) 2984, 2598, 2261, 1393, 1124, 958, 781, 664 cm^{-1}; HRMS (EI) m/z calcd for $C_8H_{10}ClO_3P$ 220.0056, found 220.0054.

*(3-Bromophenyl)phosphonic acid monoethyl ester (**1g**):* yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.50 (br s, 1H), 7.93 (d, J = 14.0 Hz, 1H), 7.72 (dd, J = 13.4 Hz, 7.6 Hz, 1H), 7.67 (d, J = 8.0 Hz, 1H), 7.33 (td, J = 7.8 Hz, 4.9 Hz, 1H). 4.14−4.07 (m, 2H), 1.33 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.4 (d, J = 2.9 Hz), 134.1 (d, J = 11.0 Hz), 131.1 (d, J = 193.7 Hz), 130.1 (d, J = 16.6 Hz), 129.8 (d, J = 9.6 Hz), 122.8 (d, J = 20.5 Hz), 62.5 (d, J = 5.9 Hz), 16.2 (d, J = 6.8 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ 18.48; IR (film) 2983, 1680, 1398, 1140, 1039, 960, 785, 572 cm^{-1}; HRMS (EI) m/z calcd for $C_8H_{10}BrO_3P$ 263.9551, found 263.9549.

*(4-Acetylphenyl)phosphonic acid monoethyl ester (**1h**):* pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.26 (s, 1H), 8.00−7.97 (m, 2H), 7.92−7.87 (m, 2H), 4.14−4.06 (m, 2H), 2.62 (s, 3H), 1.31 (d, J = 7.06 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.4, 139.8 (d, J = 3.24 Hz), 133.5 (d, J = 192.73 Hz), 131.6 (d, J = 10.44 Hz), 127.9 (d, J = 15.41 Hz), 62.4 (d, J = 6.09 Hz), 26.7, 16.2 (d, J = 6.70 Hz), 13.9, 13.8; ^{31}P NMR (121 MHz, $CDCl_3$) δ 18.99; IR (film) 2908, 1689, 1396, 1164, 1039, 993, 954, 786 cm^{-1}; HRMS (EI) m/z calcd for $C_{10}H_{13}O_4P$ 228.0551, found 228.0549.

*(2,3-Dimethylphenyl)phosphonic acid monoethyl ester (**1i**):* brown solid, mp 110−119 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.14 (s, 1H), 7.78 (dd, J = 14.5, 7.3 Hz, 1H), 7.30 (d, J = 7.5 Hz, 1H), 7.13 (td, J = 11.4, 4.3 Hz, 1H), 4.11−4.04 (m, 2H), 2.50 (d, J = 1.5 Hz, 3H), 2.30 (s, 3H), 1.31 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.1 (d, J = 10.9 Hz), 137.9 (d, J = 15.0 Hz), 134.1 (d, J = 3.0 Hz), 131.2 (d, J = 10.3 Hz), 127.4 (d, J = 189.5 Hz), 125.2 (d, J = 16.3 Hz), 61.6 (d, J = 6.0 Hz), 20.3 (d, J = 1.9 Hz), 17.7 (d, J = 4.6 Hz), 16.2 (d, J = 6.7 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ 22.82; IR (film) 2980, 2309, 1681, 1451, 1391, 1038, 983, 778 cm^{-1}; HRMS (EI) m/z calcd for $C_{10}H_{15}O_3P$ 214.0759, found 214.0757.

*(4-Methoxy-2-methylphenyl)phosphonic acid monoethyl ester (**1j**):* colorless solid, mp 95−100 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.12 (s, 1H), 7.82 (dd, J = 14.1, 8.5 Hz, 1H), 6.76−6.71 (m, 2H), 4.05 (q, J = 7.3 Hz, 2H), 3.82 (s, 3H), 2.55 (s, 3H), 1.30 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7 (d, J = 3.4 Hz), 143.9 (d, J = 12.1 Hz), 135.3 (d, J = 11.8 Hz), 118.8 (d, J = 198.0 Hz), 116.9 (d, J = 16.1 Hz), 110.2 (d, J = 16.3 Hz), 61.5 (d, J = 5.9 Hz), 55.2,

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21.4 (d, J = 3.6 Hz), 16.2 (d, J = 6.8 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ 22.63; IR (film): 2980, 2590, 2291, 1565, 1463, 1393, 1089, 982, 727 cm^{-1}; HRMS (EI) m/z calcd for $C_{10}H_{15}O_4P$ 230.0708, found 230.0710.

*(1,3-Benzodioxol-5-yl)phosphonic acid monoethyl ester (**1k**):* pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.04 (s, 1H), 7.34 (q, J = 7.42 Hz, 1H), 7.17 (d, J = 13.24 Hz, 1H), 6.84 (q, J = 3.81 Hz, 1H), 6.00 (s, 2H), 4.09−4.02 (m, 2H), 1.30 (t, J = 7.04 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.0 (d, J = 2.97 Hz), 147.7 (d, J = 23.32 Hz), 126.8 (d, J = 11.23 Hz), 121.7 (d, J = 199.76 Hz), 110.9 (d, J = 12.77 Hz), 108.4 (d, J = 19.00 Hz), 101.5, 62.0 (d, J = 5.73 Hz), 16.1 (d, J = 6.68 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ 20.85; IR (film) 2984, 2588, 1667, 1486, 1247, 1038, 962, 778 cm^{-1}; HRMS (EI) m/z calcd for $C_9H_{11}O_5P$ 230.0344, found 230.0344.

*(1-Naphthalenyl)phosphonic acid monoethyl ester (**1l**):* brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.79 (s, 1H), 8.50 (d, J = 8.36 Hz, 1H), 8.21−8.15 (m, 1H), 8.00 (d, J = 8.24 Hz, 1H), 7.89−7.86 (m, 1H), 7.59−7.51 (m, 2H), 7.48−7.43 (m, 1H), 4.12−4.05 (m, 2H), 1.27 (t, J = 7.06 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.6 (d, J = 6.05 Hz), 133.5 (d, J = 4.45 Hz), 133.4, 132.5 (d, J = 11.51 Hz), 128.6 (d, J = 1.53 Hz), 127.4, 126.7 (d, J = 4.69 Hz), 126.3, 125.0 (d, J = 190.11 Hz), 124.4 (d, J = 16.92 Hz), 62.1 (d, J = 5.77 Hz), 16.2 (d, J = 7.33 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ 21.32; IR (film) 2982, 2600, 2289, 1671, 1508, 1196, 981, 775 cm^{-1}; HRMS (EI) m/z calcd for $C_{12}H_{13}O_3P$ 236.0602, found 236.0603.

*Bis(2-methylphenyl)phosphinic acid (**4b**):* white solid, mp 166−169 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (dd, J = 7.6, 1.2 Hz, 1H), 7.87 (dd, J = 7.6, 1.2 Hz, 1H), 7.37 (t, J = 2.2 Hz, 2H), 7.21 (t, J = 3.4 Hz, 2H), 7.13 (t, J = 6.3 Hz, 2H), 2.30 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.4 (d, J = 11.2 Hz), 133.1 (d, J = 10.5 Hz), 132.0 (d, J = 2.5 Hz), 131.1 (d, J = 12.7 Hz), 131.0 (d, J = 135.1 Hz), 125.3 (d, J = 13.1 Hz), 21.1 (d, J = 4.4 Hz); ^{31}P NMR (161 MHz, $CDCl_3$) δ 77.01; IR (film) 3059, 2960, 2870, 1668, 1566, 1275, 944, 699 cm^{-1}; HRMS (EI) m/z calcd for $C_{14}H_{15}O_2P$ 246.0810, found 246.0807.

*Bis(4-methoxyphenyl)phosphinic acid (**4c**):* white solid, mp 156−159 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (dd, J = 8.8, 12.1 Hz, 4H), 7.13 (s, 1H), 6.84 (dd, J = 8.8, 2.7 Hz, 4H), 3,80 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3 (d, J = 2.5 Hz), 133.1 (d, J = 11.9 Hz), 124.4 (d, J = 147.8 Hz), 113.8 (d, J = 14.5 Hz), 55.2; ^{31}P NMR (161 MHz, $CDCl_3$) δ 33.92; IR (film) 3419, 2932, 1599, 1504, 1296, 1254, 1177, 1130, 1027, 957 cm^{-1}; HRMS (EI) m/z calcd for $C_{14}H_{15}O_4P$ 278.0708, found 278.0706.

*Bis(4-chlorophenyl)phosphinic acid (**4d**):* pale yellow solid, mp 126−129 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61−7.56 (m, 4H), 7.33−7.31 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7 (d, J = 3.6 Hz), 132.6 (d, J = 11.4 Hz), 130.6 (d, J = 143.8 Hz), 128.8 (d, J = 14.2 Hz); ^{31}P NMR (161 MHz, $CDCl_3$) δ 29.12; IR (film) 3418, 3086, 1650, 1173, 1087, 762, 549 cm^{-1}; HRMS (EI) m/z calcd for $C_{12}H_9C_{l2}O_2P$ 285.9717, found 285.9718.

*Dinaphthalen-1-ylphosphinic acid (**4e**):* white solid, mp 124−127 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, J = 8.5 Hz, 3H, −OH overlapped), 8.19 (dd, J = 7.1, 0.9 Hz, 1H), 8.15 (dd, J = 7.0, 0.9, Hz, 1H), 7.94 (d, J = 7.9 Hz, 2H), 7.81 (d, J = 8.0 Hz, 2H), 7.45−7.68 (m, 4H), 7.35−7.31 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.6, 133.5 (d, J = 3.6 Hz), 133.35 (d, J = 3.2 Hz), 133.32 (d, J = 2.6 Hz), 132.7 (d, J = 11.2 Hz), 128.7, 126.7 (d, J = 103.4 Hz), 126.6 (d, J = 5.1 Hz), 124.6, 124.4; ^{31}P NMR (161 MHz, $CDCl_3$) δ 77.01 IR (film) 3434, 1651, 1334, 1152, 1026, 997, 944, 773 cm^{-1}; HRMS (EI) m/z calcd for $C_{20}H_{15}O_2P$ 318.0810, found 318.0810.

*Mesityl(phenyl)phosphinic acid (**4f**):* white solid, mp 155−157 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (s, 1H), 7.64−7.58 (m, 2H), 7.45−7.41 (m, 1H), 7.35−7.31 (m, 2H), 6.85 (s, 1H), 2.48 (s, 6H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4 (d, J = 11.7 Hz), 141.8 (d, J = 2.6 Hz), 135.2 (d, J = 135.9 Hz), 131.4 (d, J = 2.7 Hz), 130.6 (d, J = 13.2 Hz), 130.1 (d, J = 11.6 Hz), 128.3 (d, J = 13.5 Hz), 124.9 (d, J = 135.2 Hz), 23.5 (d, J = 3.5 Hz), 21.1; ^{31}P NMR (161 MHz, $CDCl_3$) δ 39.55; IR (film) 3421, 2971, 1606, 1437, 1167, 949 cm^{-1}; HRMS (EI) m/z calcd for $C_{15}H_{17}O_2P$ 260.0966, found 260.0963.

*4-(Ethoxy(hydroxy)phosphoryl)benzoic acid (**4g**):* white solid, mp 167−170 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.05−8.03 (m, 2H), 7.83−7.78 (m, 2H), 3.94−3.86 (m, 2H), 1.18 (t, J = 7.04 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.7, 135.8 (d, J = 180.78 Hz), 133.4 (d, J = 3.02 Hz), 131.1 (d, J = 10.09 Hz), 129.0 (q, J = 14.29 Hz), 60.8 (d, J = 5.18 Hz), 16.1 (d, J = 6.20 Hz); ^{31}P NMR (121 MHz, DMSO-d_6) δ 13.46; IR (film) 2850, 1681, 1393, 1205, 1161, 1041, 956, 762 cm^{-1}; HRMS (EI) m/z calcd for $C_9H_{11}O_5P$ 230.0344, found 230.0346

*(1-Phenylethenyl)phosphonic acid monoethyl ester (**4h**):* pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.56 (s, 1H), 7.55−7.53 (m, 2H), 7.37−7.31 (m, 3H), 6.31 (dd, J = 22.48 Hz, 1.36 Hz, 1H), 6.12 (dd, J = 46.53 Hz, 1.36 Hz, 1H), 4.09−4.02 (m, 2H), 1.26 (d, J = 7.06 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.7 (d, J = 180.91 Hz), 136.3 (d, J = 12.33 Hz), 131.0 (d, J = 7.94 Hz), 128.4, 128.3, 127.5 (d, J = 5.88 Hz), 62.2 (d, J = 6.10 Hz), 16.1 (d, J = 6.47 Hz); ^{31}P NMR (161 MHz, $CDCl_3$) δ 19.55; IR (film) 2983, 2599, 2275, 1676, 1493, 1202, 1040, 959, 778 cm^{-1}; HRMS (EI) m/z calcd for $C_{10}H_{13}O_3P$ 212.0602, found 212.0601

Representative Procedure for the Preparation of Alkynes 2.[11] *1,2-Di-m-tolylethyne (**2b**):* R_f = 0.4 (hexane); white solid, mp 115−118 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.32 (m, 4H), 7.23 (t, J = 7.60 Hz, 2H), 7.13 (d, J = 7.65 Hz, 2H), 2.34 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.0, 132.2, 129.1, 128.7, 128.3, 123.2, 89.2, 21.3; IR (film) 3038, 2976, 2251, 2208, 1602, 1579 cm^{-1}; HRMS (EI) m/z calcd for $C_{16}H_{14}$: 206.2824, found 206.2827.

*1,2-Di-p-tolylethyne (**2c**):* R_f = 0.4 (hexane); white solid, mp 138−140 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 8.12 Hz, 4H), 7.15 (d, J = 7.92 Hz, 4H), 2.36 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.1, 131.4, 129.1, 120.4, 88.9, 21.5; IR (film) 3026, 2915, 2299, 2136, 1654, 1638 cm^{-1}; HRMS (EI) m/z calcd for $C_{16}H_{14}$ 206.2824, found 206.2826.

*1,2-Bis(4-methoxyphenyl)ethyne (**2d**):* R_f = 0.3 (EtOAc/hexane 1/15); pale yellow solid, mp 147−148 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 8.92 Hz, 4H), 6.86 (d, J = 8.92 Hz, 4H), 3.82 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 132.8, 115.7, 113.9, 87.9, 55.3; IR (film) 2840, 2254, 1244, 1026 cm^{-1}; HRMS (EI) m/z calcd for $C_{16}H_{14}O_2$: 238.0994, found 238.0992.

*1,2-Bis(3-chlorophenyl)ethyne (**2e**):* R_f = 0.6 (hexane); white solid, mp 81−82 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52−7.51 (m, 2H), 7.42−7.39 (m, 2H), 7.36−7.32 (m, 2H), 7.30−7.27 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.3, 131.5, 129.8, 129.6, 128.8, 124.5, 89.0; IR (film) 2328, 2303, 1591, 1556, 909, 788 cm^{-1}; HRMS (EI) m/z calcd for $C_{14}H_8Cl_2$ 246.0003, found 246.0005.

*1,2-Bis(4-chlorophenyl)ethyne (**2f**):* R_f = 0.6 (hexane); white solid, mp 174−176 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46−7.43 (m, 4H), 7.34−7.31 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.5, 132.8, 128.8, 121.4, 89.1; IR (film) 2348, 2309, 683 cm^{-1}; HRMS (EI) m/z calcd for $C_{14}H_8Cl_2$ 246.0003, found 246.0000.

*3,4-Bis(3-methylphenyl)-1-ethoxybenz[c-1,2]oxaphosphinine 1-oxide (**3b**):* R_f = 0.3 (EtOAc/hexane 1/3); pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97−7.91 (m, 1H), 7.49−7.39 (m, 2H), 7.26−7.15 (m, 4H), 7.02−6.94 (m, 5H), 4.30−4.17 (m, 2H), 2.31 (s, 3H), 2.20 (s, 3H), 1.31 (t, J = 7.06 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.7 (d, J = 10.55 Hz), 140.4 (d, J = 6.91 Hz), 138.5, 137.2, 136.0, 134.3 (d, J = 5.40 Hz), 132.7 (d, J = 2.87 Hz), 131.9, 129.34, 129.30, 129.26, 129.21, 128.7, 128.5, 127.4 (d, J = 15.74 Hz), 127.3, 127.2 (d, J = 11.92 Hz), 126.0, 120.8 (d, J = 181.33 Hz), 119.7 (d, J = 11.74 Hz), 62.9 (d, J = 6.60 Hz), 21.3 (d, J = 6.79 Hz), 16.4 (d, J = 5.94 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ 10.65; IR (film) 2980, 1591, 1469, 1275, 1031, 963, 772, 701 cm^{-1}; HRMS (EI) m/z calcd for $C_{24}H_{23}O_3P$ 390.1385, found 390.1383.

*3,4-Bis(4-methylphenyl)-1-ethoxybenz[c-1,2]oxaphosphinine 1-oxide (**3c**):* R_f = 0.3 (EtOAc/hexane 1/3); yellow solid, mp 44−47 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96−7.90 (m, 1H), 7.46−7.37 (m, 2H), 7.25−7.07 (m, 6H), 6.97−6.94 (m, 3H), 4.30−4.16 (m, 2H), 2.38 (s, 3H), 2.26 (s, 3H), 1.30 (t, J = 7.06 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8 (d, J = 10.47 Hz), 140.6 (d, J = 6.75 Hz), 138.4, 137.5, 133.1 (d, J = 0.94 Hz), 132.7 (d, J = 2.35 Hz), 131.7 (d, J = 5.58 Hz), 131.3, 129.6, 129.2 (d, J = 9.05 Hz), 128.7, 128.4, 127.3 (d, J = 15.70 Hz), 127.0 (d, J = 12.20 Hz), 120.8 (d, J = 181.35 Hz),

119.2 (d, J = 11.75 Hz), 62.8 (d, J = 6.67 Hz), 21.2 (d, J = 6.82 Hz), 16.4 (d, J = 5.97 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ 10.66; IR (film) 2981, 2239, 1606, 1469, 1274, 1030, 955, 773 cm^{-1}; HRMS (EI) m/z calcd for $C_{24}H_{23}O_3P$ 390.1385, found 390.1382.

3,4-Bis(4-methoxyphenyl)-1-ethoxybenz[c-1,2]oxaphosphinine 1-oxide (**3d**): R_f = 0.3 (EtOAc/hexane 1/1); pale yellow solid, mp 114−116 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95−7.89 (m, 1H), 7.48−7.43 (m, 1H), 7.41−7.37 (m, 1H), 7.19 (dt, J = 9.17 Hz, 2.56 Hz, 2H), 7.14−7.10 (m, 2H), 7.00−6.96 (m, 1H), 6.93−6.89 (m, 2H), 7.19 (dt, J = 9.20 Hz, 2.52 Hz, 2H), 4.30−4.15 (m, 2H), 3.84 (s, 3H), 3.75 (s, 3H), 1.31 (t, J = 4.82 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 159.1, 147.7 (d, J = 10.65 Hz), 140.8 (d, J = 6.99 Hz), 132.7 (d, J = 2.35 Hz), 132.6, 130.2, 129.2 (d, J = 9.13), 128.4, 127.2 (d, J = 15.55 Hz), 127.0, 126.9 (d, J = 12.19 Hz), 120.7 (d, J = 181.49 Hz) 118.2 (d, J = 11.67 Hz), 114.4, 113.1, 62.8 (d, J = 6.60 Hz), 55.2 (d, J = 9.28 Hz), 16.4 (d, J = 5.86 Hz), 14.1, 11.7; ^{31}P NMR (121 MHz, $CDCl_3$) δ 10.73; IR (film) 2907, 1605, 1508, 1252, 1029, 954, 827, 774 cm^{-1}; HRMS (EI) m/z calcd for $C_{24}H_{23}O_5P$ 422.1283, found 422.1282.

3,4-Bis(3-chlorophenyl)-1-ethoxybenz[c-1,2]oxaphosphinine 1-oxide (**3e**): R_f = 0.3 (EtOAc/hexane =1/1); pale yellow solid, mp 134−137 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99−7.93 (m, 1H), 7.54−7.45 (m, 2H), 7.39−7.30 (m, 3H), 7.26−7.18 (m, 2H), 7.11−7.02 (m, 3H), 6.95−6.91 (m, 1H), 4.35−4.21 (m, 2H), 1.34 (t, J = 7.06 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.6 (d, J = 10.34 Hz), 139.2 (d, J = 6.75 Hz), 137.4, 135.8 (d, J = 5.70 Hz), 134.9, 133.9, 133.0 (d, J = 3.33 Hz), 131.3, 130.3, 129.7, 129.5 (d, J = 9.01 Hz), 129.0 (d, J = 6.60 Hz), 128.7, 128.5, 128.2 (d, J = 15.75 Hz), 127.09, 127.00, 126.9, 121.0 (d, J = 182.26 Hz), 119.5 (d, J = 13.04 Hz), 63.2 (d, J = 6.69 Hz), 16.4 (d, J = 5.86 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ 10.28; IR (film) 2981, 2242, 1592, 1470, 1276, 1194, 1028, 974, 776 cm^{-1}; HRMS (EI) m/z calcd for $C_{22}H_{17}Cl_2O_3P$ 430.0292, found 430.0290.

3,4-Bis(4-chlorophenyl)-1-ethoxybenz[c-1,2]oxaphosphinine 1-oxide (**3f**): R_f = 0.3 (EtOAc/hexane 1/3); pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98−7.92 (m, 1H), 7.52−7.44 (m, 1H), 7.37 (d, J = 7.72 Hz, 2H), 7.21−7.12 (m, 6H), 6.92 (t, J = 7.40 Hz, 1H), 4.34−4.20 (m, 2H), 1.32 (t, J = 7.08, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.9 (d, J = 10.35 Hz), 139.5 (d, J = 6.81 Hz), 134.8, 134.2 (d, J = 1.98 Hz), 133.0 (d, J = 2.63 Hz), 132.8, 132.7 (d, J = 5.62 Hz), 130.1, 129.5, 129.4, 128.2, 128.0 (d, J = 15.54 Hz), 126.9 (d, J = 11.93 Hz), 121.9, 120.1, 119.2 (d, J = 12.11 Hz), 63.2 (d, J = 6.63 Hz), 16.5 (d, J = 5.83 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ 10.38; IR (film) 3062, 2982, 1487, 1273, 1092, 1028, 954 cm^{-1}; HRMS (EI) m/z calcd for $C_{22}H_{17}Cl_2O_3P$ 430.0292, found 430.0290.

3,4-Diethyl-1-ethoxybenz[c-1,2]oxaphosphinine 1-oxide (**3g**): R_f = 0.2 (EtOAc/hexane 1/3); pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89−7.82 (m, 1H), 7.63−7.58 (m, 1H), 7.45 (t, J = 7.26 Hz, 1H), 7.40−7.35 (m, 1H), 4.23−4.09 (m, 2H), 2.60−2.42 (m, 4H), 1.31 (t, J = 7.25 Hz, 3H), 1.23 (t, J = 7.50 Hz, 3H), 1.16 (t, J = 7.25 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.7 (d, J = 10.98 Hz), 138.8 (d, J = 6.71 Hz), 132.9 (d, J = 2.60 Hz), 129.6 (d, J = 8.88 Hz), 126.6 (d, J = 15.60 Hz), 123.7 (d, J = 12.46 Hz), 121.3 (d, J = 179.67 Hz) 114.8 (d, J = 12.47 Hz), 62.5 (d, J = 6.46 Hz), 25.3 (d, J = 5.41 Hz), 20.8, 16.4 (d, J = 6.06 Hz), 14.1, 11.7; ^{31}P NMR (121 MHz, $CDCl_3$) δ 6.23; IR (film) 2971, 1631, 1470, 1270, 1030, 982, 856, 774 cm^{-1}; HRMS (EI) m/z calcd for $C_{14}H_{19}O_3P$ 266.1072, found 266.1073.

3,4-Dibutyl-1-ethoxybenz[c-1,2]oxaphosphinine 1-oxide (**3h**): R_f = 0.3 (EtOAc/hexane 1/3); pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87−7.82 (m, 1H), 7.62−7.57 (m, 1H), 7.44−7.35 (m, 2H), 4.22−4.08 (m, 2H), 2.58−2.41 (m, 2H), 1.69−1.61 (m, 2H), 1.53−1.36 (m, 6H), 1.30 (t, J = 7.06 Hz, 3H), 0.95 (dt, J = 7.25 Hz, 1.62 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.8 (d, J = 10.97 Hz), 139.0 (d, J = 6.77 Hz), 132.8 (d, J = 2.32 Hz), 129.5 (d, J = 9.16 Hz), 126.6 (d, J = 15.63 Hz), 123.9 (d, J = 12.44 Hz), 121.3 (d, J = 179.63 Hz), 114.1 (d, J = 12.03 Hz), 62.4 (d, J = 6.47 Hz), 31.7 (d, J = 5.29 Hz), 31.5, 29.2, 27.4, 22.7, 22.3, 16.4, 16.3, 13.9 (d, J = 1.33 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ 10.84; IR (film) 2930, 1630, 1468, 1270, 1031, 960, 774 cm^{-1}; HRMS (EI) m/z calcd for $C_{18}H_{27}O_3P$ 322.1698, found 322.1700.

3-Phenyl-4-methyl-1-ethoxybenz[c-1,2]oxaphosphinine 1-oxide (**3i**): R_f = 0.2 (EtOAc/hexane 1/3); pale yellow solid, mp 106−108 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94−7.88 (m, 1H), 7.69−7.65 (m, 1H), 7.56−7.52 (m, 3H), 7.49−7.39 (m, 4H), 4.28−4.19 (m, 2H), 2.21 (d, J = 0.92, 3H), 1.33 (t, J = 7.08 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5 (d, J = 10.26 Hz), 140.0 (d, J = 7.21 Hz), 134.7 (d, J = 5.80 Hz), 133.0 (d, J = 2.35), 129.4, 129.3 (d, J = 8.85 Hz), 129.1, 128.1, 127.4 (d, J = 15.54 Hz), 124.7 (d, J = 12.38 Hz), 121.4 (d, J = 180.04 Hz), 111.3 (d, J = 11.69 Hz), 62.9 (d, J = 6.52 Hz), 16.4 (d, J = 6.02 Hz), 15.6; ^{31}P NMR (121 MHz, $CDCl_3$) δ 10.71; IR (film) 2983, 1629, 1473, 1269, 1030, 1007, 962, 760 cm^{-1}; HRMS (EI) m/z calcd for $C_{17}H_{17}O_3P$ 300.0915, found 300.0914.

3,4-Diphenyl-1-ethoxy-8-methoxybenz[c-1,2]oxaphosphinine 1-oxide (**3j**): R_f = 0.3 (EtOAc/hexane 1/1); white solid, mp 164−166 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (t, J = 8.22 Hz, 1H), 7.35−7.33 (m, 3H), 7.24−7.10 (m, 7H), 6.91−6.88 (m, 1H), 6.57−6.54 (m, 1H), 4.41−4.33 (m, 2H), 4.00 (s, 3H), 1.41 (t, J = 7.08 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 147.9 (d, J = 9.91 Hz), 141.9 (d, J = 5.18 Hz), 136.3, 134.6 (d, J = 6.00 Hz), 133.9, 131.7, 129.1, 128.8, 128.5, 127.7, 127.5, 120.0 (d, J = 12.06 Hz), 118.3 (d, J = 12.01 Hz), 109.5 (d, J = 9.22 Hz), 109.4 (d, J = 178.10), 63.9 (d, J = 6.18 Hz), 56.2, 16.5 (d, J = 6.66 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ 8.67; IR (film) 2982, 1561, 1465, 1271, 1035, 974 cm^{-1}; HRMS (EI) m/z calcd for $C_{23}H_{21}O_4P$ 392.1177, found 392.1178.

3,4-Diethyl-1-ethoxy-8-methoxybenz[c-1,2]oxaphosphinine 1-oxide (**3k**): R_f = 0.3 (EtOAc/hexane 1/1); colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (t, J = 8.22 Hz, 1H), 7.06−7.02 (m, 1H), 6.87−6.83 (m, 1H), 4.27−4.20 (m, 2H), 3.95 (s, 3H), 2.53−2.45 (m, 4H), 1.36 (t, J = 7.08 Hz, 3H), 7.23 (t, J = 7.50 Hz, 3H), 1.13 (t, J = 7.50 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 151.8 (d, J = 10.54 Hz), 140.8 (d, J = 5.16 Hz), 134.0, 116.6 (d, J = 12.70 Hz), 113.4 (d, J = 11.94 Hz), 109.9 (d, J = 176.70 Hz), 108.6 (d, J = 9.36 Hz), 63.4 (d, J = 6.25 Hz), 56.0, 25.4 (d, J = 5.67 Hz), 21.0, 16.4 (d, J = 6.74 Hz), 14.2, 11.7; ^{31}P NMR (121 MHz, $CDCl_3$) δ 8.84; IR (film) 2972, 1631, 1265, 1028, 948 cm^{-1}; HRMS (EI) m/z calcd for $C_{15}H_{21}O_4P$ 296.1177, found 296.1177.

R_f = 0.2 (EtOAc/hexane 1/3); pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) data for major isomer δ 7.49−7.34 (m, 2H), 7.18−7.13 (m, 1H), 4.26−4.11 (m, 2H), 3.88 (s, 3H), 2.65−2.38 (m, 4H), 1.34 (t, J = 7.08 Hz, 3H), 1.24 (t, J = 7.44 Hz, 3H), 1.17 (t, J = 7.50 Hz, 3H), data for minor isomer δ 7.49−7.34 (m, 2H), 7.18−7.13 (m, 1H), 4.26−4.11 (m, 2H), 3.88 (s, 3H), 2.65−2.38 (m, 4H), 1.33 (t, J = 7.08 Hz, 3H), 1.24 (t, J = 7.44 Hz, 3H), 1.10 (t, J = 7.50 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0 (d, J = 19.07 Hz), 155.8 (d, J = 17.38 Hz), 150.2 (d, J = 10.30 Hz), 149.7 (d, J = 11.09 Hz), 131.7 (d, J = 6.16 Hz), 128.3 (d, J = 18.99 Hz), 127.9 (d, J = 7.39 Hz), 125.6 (d, J = 7.45 Hz), 123.9, 123.3, 121.5 (d, J = 8.81 Hz), 120.3 (d, J = 2.88 Hz), 116.7 (d, J = 13.07 Hz), 116.0 (d, J = 2.96 Hz), 114.6 (d, J = 11.74 Hz), 112.7 (d, J = 10.19 Hz), 62.6 (d, J = 6.31 Hz), 62.5 (d, J = 6.51 Hz), 55.6, 55.5, 25.0 (d, J = 5.08 Hz), 24.9 (d, J = 4.50 Hz), 22.6, 20.9, 16.4 (d, J = 5.87 Hz), 16.3 (d, J = 6.65 Hz), 14.8, 14.2, 11.9, 11.5; ^{31}P NMR (121 MHz, $CDCl_3$) δ 11.82, 10.90; IR (film) 2971, 1464, 1268, 1030, 980 cm^{-1}; HRMS (EI) m/z calcd for $C_{15}H_{21}O_4P$ 296.1177, found 296.1179.

3,4-Diethyl-1-ethoxy-8-phenylbenz[c-1,2]oxaphosphinine 1-oxide (**3n**): R_f = 0.3 (EtOAc/hexane 1/4); pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60−7.55 (m, 3H), 7.48−7.37 (m, 4H), 7.25−7.22 (m, 1H), 3.81−3.71 (m, 1H), 3.51−3.41 (m, 1H), 2.66−2.39 (m, 4H), 1.24−1.19 (m, 6H), 0.94 (t, J = 7.06 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6 (d, J = 9.69 Hz), 144.9 (d, J = 8.69 Hz), 141.2 (d, J = 5.14 Hz), 140.0 (d, J = 7.18 Hz), 131.9 (d, J = 2.22 Hz), 129.2, 129.0 (d, J = 14.18 Hz), 128.0, 127.8, 123.0 (d, J = 12.29 Hz), 121.2 (d, J = 174.32 Hz), 115.1 (d, J = 12.10 Hz), 62.9 (d, J = 6.69 Hz), 25.2 (d, J = 4.75 Hz), 21.4, 15.8 (d, J = 7.10 Hz), 14.4, 11.5; ^{31}P NMR (121 MHz, $CDCl_3$) δ 9.41; IR (film) 2971, 1641, 1455, 1258, 1035, 981 cm^{-1}; HRMS (EI) m/z calcd for $C_{20}H_{23}O_3P$ 342.1385, found 342.1388.

3,4-Diphenyl-1-ethoxy-6-fluorobenz[c-1,2]oxaphosphinine 1-oxide (**3o**): R_f = 0.2 (EtOAc/hexane 1/3); pale yellow solid, mp 126−129 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98−7.91 (m, 1H), 7.39−7.35 (m, 3H), 7.26−7.10 (m, 8H), 6.67−6.62 (m, 1H), 4.33−4.19 (m, 2H),

1.32 (t, J = 7.06 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8 (d, J = 3.69 Hz), 164.3 (d, J = 2.55 Hz), 148.9 (d, J = 10.41), 143.4 (t, J = 8.96 Hz), 135.4, 134.1 (d, J = 3.68 Hz), 132.0 (t J = 9.85 Hz), 131.4, 129.1, 128.8 (d, J = 1.72 Hz), 128.2, 127.7, 119.2 (dd, J = 11.14 Hz, 2.19 Hz), 116.9 (dd, J = 186.17 Hz, 12.02 Hz), 115.1 (q, J = 13.08 Hz), 114.0 (q, J = 12.42 Hz), 63.1 (d, J = 6.61 Hz), 16.4 (d, J = 5.94 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ 7.53; IR (film) 2983, 1593, 1470, 1269, 1213, 1025, 974, 753 cm^{-1}; HRMS (EI) m/z calcd for $C_{22}H_{18}FO_3P$ 380.0978, found 380.0979.

*3,4-Diethyl-1-ethoxy-6-fluorobenz[c-1,2]oxaphosphinine 1-oxide (**3p**):* R_f = 0.3 (EtOAc/hexane 1/5); Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88−7.81 (m, 1H), 7.14−7.05 (m, 2H), 4.24−4.12 (m, 2H), 1.32 (t, J = 4.92 Hz, 3H), 1.23 (t, J = 7.50 Hz, 3H), 1.16 (t, J = 7.54 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1 (d, J = 4.28 Hz), 164.6 (d, J = 3.65 Hz), 153.0 (d, J = 10.84 Hz), 142.0 (t, J = 8.43 Hz), 132.2 (t, J = 10.22 Hz), 117.4 (dd J = 183.78 Hz, 9.85 Hz), 114.1 (q, J = 12.92 Hz), 110.8 (q, J = 12.38 Hz), 62.7 (d, J = 6.51 Hz), 25.4 (d, J = 5.86 Hz), 20.9, 16.4 (d, J = 6.50 Hz), 14.0, 11.6; ^{31}P NMR (121 MHz, $CDCl_3$) δ 10.37; IR (film) 2973, 1600, 1474, 1273, 1162, 1031, 959, 828, 758 cm^{-1}; HRMS (EI) m/z calcd for $C_{14}H_{18}FO_3P$ 284.0978, found 284.0980.

*3,4-Diphenyl-1-ethoxy-8-chlorobenz[c-1,2]oxaphosphinine 1-oxide (**3q**):* R_f = 0.3 (EtOAc/hexane 1/3); pale yellow solid, mp 168−171 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40−7.33 (m, 5H), 7.25−7.11 (m, 7H), 6.90−6.87 (m, 1H), 4.44−4.37 (m, 2H), 1.43 (t, J = 7.08, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2 (d, J = 10.55 Hz), 142.6 (d, J = 5.69 Hz), 136.2 (d, J = 1.40 Hz), 135.9, 134.1 (d, J = 6.02 Hz), 133.2 (d, J = 1.64 Hz), 131.6, 129.0, 128.95, 128.9, 128.8, 128.1, 127.7, 125.9 (d, J = 11.26 Hz), 120.3 (d, J = 183.80 Hz), 118.4 (d, J = 11.27 Hz), 64.3 (d, J = 6.71 Hz), 16.4 (d, J = 6.61 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ 5.33; IR (film) 3057, 2981, 1443, 1266, 1026, 969 cm^{-1}; HRMS (EI) m/z calcd for $C_{22}H_{18}ClO_3P$ 396.0682, found 396.0683.

*3,4-Diethyl-1-ethoxy-8-chlorobenz[c-1,2]oxaphosphinine 1-oxide (**3r**):* R_f = 0.3 (EtOAc/hexane 1/3); pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (t, J = 8.06 Hz, 1H), 7.37−7.34 (m, 2H), 4.33−4.24 (m, 2H), 2.55−2.48 (m, 4H), 1.40 (t, J = 7.08 Hz, 3H), 1.24 (t, J = 7.50 Hz, 3H), 1.14 (t, J = 7.50 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.1 (d, J = 11.27 Hz), 141.4 (d, J = 5.66 Hz), 136.3 (d, J = 1.82 Hz), 133.3 (d, J = 1.80 Hz), 128.1 (d, J = 10.35 Hz), 122.5 (d, J = 11.18 Hz), 120.8 (d, J = 182.47 Hz), 113.7 (d, J = 11.66 Hz), 63.8 (d, J = 6.78 Hz), 25.4 (d, J = 5.41 Hz), 21.1 16.3 (d, J = 6.65 Hz), 14.1, 11.6; ^{31}P NMR (121 MHz, $CDCl_3$) δ 5.49; IR (film) 2972, 1638, 1445, 1267, 1031, 797 cm^{-1}; HRMS (EI) m/z calcd for $C_{14}H_{18}ClO_3P$ 300.0682, found 300.0682.

*3,4-Diethyl-1-ethoxy-7-bromobenz[c-1,2]oxaphosphinine 1-oxide (**3s**):* R_f = 0.3 (EtOAc hexane 1/4); pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, J = 2.20 Hz, J = 15.16 Hz, 1H), 7.71−7.69 (m, 1H), 7.33−7.28 (m, 1H), 4.23−4.16 (m, 2H), 2.60−2.41 (m, 4H), 1.34 (t, J = 7.08 Hz, 3H), 1.23 (t, J = 7.50 Hz, 3H), 1.14 (t, J = 7.52 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.2 (d, J = 11.03 Hz), 137.6 (d, J = 6.48 Hz), 135.9 (d, J = 2.68 Hz), 132.2 (d, J = 9.93 Hz), 125.7 (d, J = 13.42 Hz), 123.5 (d, J = 179.0 Hz), 120.3 (d, J = 20.51 Hz), 114.5 (d, J = 11.76 Hz), 63.0 (d, J = 6.53 Hz), 25.3 (d, J = 5.24 Hz), 20.9, 16.4 (d, J = 6.07), 14.1, 11.7; ^{31}P NMR (121 MHz, $CDCl_3$) δ 8.45; IR (film) 2970, 1468, 1265, 1028, 965 cm^{-1}; HRMS (EI) m/z calcd for $C_{14}H_{18}BrO_3P$ 344.0177, found 344.0180.

*3,4-Diphenyl-1-ethoxy-6-acetylbenz[c-1,2]oxaphosphinine 1-oxide (**3t**):* R_f = 0.3 (EtOAc/hexane 1/5); yellow solid, mp 97−102 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08−8.02 (m, 1H), 7.98−7.95 (m, 1H), 7.53−7.51 (m, 1H), 7.39−7.37 (m, 3H), 7.26−7.13 (m, 7H), 4.36−4.22 (m, 2H), 2.44 (s, 3H), 1.33 (t, J = 7.08 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.2, 148.6 (d, J = 10.40 Hz), 140.8 (d, J = 7.06 Hz), 140.4 (d, J = 2.81), 135.3, 134.1 (d, J = 5.73 Hz), 131.3, 129.8 (d, J = 9.35 Hz), 129.1, 128.8, 128.3, 127.7, 126.7 (d, J = 2.87 Hz), 126.6, 124.9 (d, J = 180.38 Hz), 119.6 (d, J = 11.36 Hz), 63.4 (d, J = 6.64 Hz), 26.6, 16.4 (d, J = 5.85 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ 9.07; IR (film) 3059, 2984, 2243, 1692, 1398, 1277, 1185, 1024, 955, 751 cm^{-1}; HRMS (EI) m/z calcd for $C_{24}H_{21}O_4P$ 404.1177, found 404.1178.

*3,4-Diphenyl-1-ethoxy-7,8-dimethylbenz[c-1,2]oxaphosphinine 1-oxide (**3u**):* R_f = 0.3 (EtOAc/hexane 1/3); white solid, mp 110−113 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35−7.33 (m, 3H), 7.22−7.11 (m, 8H), 6.69 (t, J = 7.34, 1H), 4.33−4.15 (m, 2H), 2.70 (s, 3H), 2.32 (s, 3H), 1.35 (t, J = 7.06 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.2 (d, J = 10.65 Hz), 139.5 (d, J = 9.52 Hz), 138.9 (d, J = 7.42 Hz), 137.2 (d, J = 14.80 Hz), 136.7, 134.5 (d, J = 5.61 Hz), 134.1 (d, J = 2.63 Hz), 131.7, 128.8, 128.7, 128.3, 127.7, 127.6, 125.3 (d, J = 13.15 Hz), 120.9, 119.4 (d, J = 55.97 Hz), 62.69 (d, J = 7.20 Hz), 20.22, 18.42 (d, J = 5.61 Hz), 16.39 (d, J = 6.31 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ 10.93; IR (film) 3054, 2980, 1464, 1260, 1029, 752 cm^{-1}; HRMS (EI) m/z calcd for $C_{24}H_{23}O_3P$ 390.1385, found 390.1387.

*3,4-Diethyl-1-ethoxy-7,8-dimethylbenz[c-1,2]oxaphosphinine 1-oxide (**3v**):* R_f = 0.3 (EtOAc/hexane 1/3); colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, J = 8.20 Hz, 1H), 7.20 (t, J = 7.42 Hz, 1H), 4.22−4.03 (m, 2H), 2.62 (d, J = 1.68 Hz, 3H), 2.53−2.45 (m, 4H), 2.31 (s, 3H), 1.33 (t, J = 7.06 Hz, 3H), 1.22 (t, J = 7.50 Hz, 3H), 1.13 (t, J = 7.50 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.1 (d, J = 11.12 Hz), 139.8 (d, J = 9.56 Hz), 137.4 (d, J = 7.34 Hz), 136.0 (d, J = 15.05 Hz), 134.3 (d, J = 2.35 Hz), 121.7 (d, J = 13.74 Hz), 120.4 (d, J = 174.67 Hz), 114.3 (d, J = 11.74 Hz), 62.3 (d, J = 6.83 Hz), 25.1 (d, J = 5.28 Hz), 21.1, 20.1 (d, J = 1.28 Hz), 18.3 (d, J = 5.70 Hz), 16.3 (d, J = 6.53 Hz), 14.3, 11.9; ^{31}P NMR (121 MHz, $CDCl_3$) δ 11.11; IR (film) 2971, 1466, 1263, 1033, 964 cm^{-1}; HRMS (EI) m/z calcd for $C_{16}H_{23}O_3P$ 294.1385, found 294.1386.

*3,4-Diphenyl-1-ethoxy-6-methoxy-8-methylbenz[c-1,2]-oxaphosphinine 1-oxide (**3w**):* R_f = 0.2 (EtOAc/hexane 1/3); white solid, mp 96−99 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, J = 1.76 Hz, 3H), 7.23−7.10 (m, 7H), 6.75 (t, J = 2.82, 1H), 6.30−6.28 (m, 1H), 4.31−4.14 (m, 2H), 3.64 (s, 3H), 2.75 (s, 3H), 1.34 (t, J = 7.08, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 126.5 (d, J = 2.98 Hz), 147.6 (d, J = 10.32 Hz), 143.7 (d, J = 10.80 Hz), 143.2 (d, J = 8.73 Hz), 136.5, 134.6 (d, J = 5.82 Hz), 131.6, 128.9, 128.4, 127.8, 127.6, 119.3 (d, J = 11.24 Hz), 115.5 (d, J = 5.72 Hz), 112.5, 110.9 (d, J = 12.91 Hz), 110.7, 62.6 (d, J = 6.92 Hz), 55.1, 21.9 (d, J = 4.77 Hz), 16.4 (d, J = 6.29 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ 11.14; IR (film) 2980, 1589, 1262, 1029, 862 cm^{-1}; HRMS (EI) m/z calcd for $C_{24}H_{23}O_4P$ 406.1334, found 406.1333.

*3,4-Diethyl-1-ethoxy-6-methoxy-8-methylbenz[c-1,2]-oxaphosphinine 1-oxide (**3x**):* R_f = 0.2 (EtOAc/hexane 1/3); colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.80−6.78 (m, 1H), 6.71−6.70 (m, 1H), 4.20−4.02 (m, 2H), 3.86 (s, 3H), 2.67 (d, J = 1.60 Hz, 3H), 2.56−2.41 (m, 4H), 1.32 (t, J = 7.08 Hz, 3H), 1.23 (t, J = 7.50 Hz, 3H), 1.14 (t, J = 7.50 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8 (d, J = 3.00 Hz), 151.6 (d, J = 10.99 Hz), 143.9 (d, J = 10.50 Hz), 141.7 (d, J = 8.65 Hz), 114.3 (d, J = 15.74 Hz), 114.1 (d, J = 11.64 Hz), 112.0 (d, J = 182.57 Hz), 107.7 (d, J = 13.38 Hz), 62.2 (d, J = 6.76 Hz), 55.2, 25.4 (d, J = 5.34 Hz), 22.0 (d, J = 4.59 Hz), 21.3, 16.4 (d, J = 6.53 Hz), 14.2, 11.9; ^{31}P NMR (121 MHz, $CDCl_3$) δ 11.24; IR (film) 2969, 1591, 1261, 1033, 959 cm^{-1}; HRMS (EI) m/z calcd for $C_{16}H_{23}O_4P$ 310.1334, found 310.1331.

*3,4-Diethyl-7,8-(methylenedioxy)-1-ethoxybenz[c-1,2]-oxaphosphinine 1-oxide (**3y**):* R_f = 0.3 (EtOAc/hexane =1/7); pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (q, J = 7.72 Hz, 1H), 6.87 (q, J = 3.69 Hz, 1H), 6.02 (dd, J = 6.30 Hz, 1.38 Hz, 2H), 4.18−4.07 (m, 2H), 2.72−2.37 (m, 4H), 1.29 (t, J = 7.06 Hz, 3H), 1.21 (t, J = 7.48 Hz, 3H), 1.10 (t, J = 7.36 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.6 (d, J = 3.89 Hz), 151.5 (d, J = 10.38 Hz), 142.3 (d, J = 20.12 Hz), 125.1 (d, J = 10.05), 122.2 (d, J = 9.08 Hz), 115.6 (d, J = 186.93 Hz), 113.9 (d, J = 11.93 Hz), 107.8 (d, J = 19.15 Hz), 100.9, 62.3 (d, J = 6.43 Hz), 24.8 (d, J = 4.85 Hz), 21.5, 16.3 (d, J = 6.16 Hz), 14.8, 11.7; ^{31}P NMR (121 MHz, $CDCl_3$) δ 11.44; IR (film) 2976, 1632, 1440, 1271, 1192, 1035, 905, 774 cm^{-1}; HRMS (EI) m/z calcd for $C_{15}H_{19}O_5P$ 310.0970, found 310.0970.

*3,4-Diphenyl-1-ethoxynaphth[c-1,2]oxaphosphinine 1-oxide (**3z**):* R_f = 0.3 (EtOAc/hexane 1/4); pale yellow solid, mp 144−148 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (d, J = 8.48 Hz, 1H), 7.88−7.82 (m, 2H), 7.69−7.65 (m, 1H), 7.58−7.54 (m, 1H), 7.40−7.39 (m, 3H), 7.29−7.15 (m, 7H), 7.08−7.04 (m, 1H),

4.37−4.21 (m, 2H), 1.33 (t, J = 7.08, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.4 (d, J = 11.31 Hz), 140.6 (d, J = 5.97 Hz), 136.4, 134.3, 133.1 (d, J = 2.89 Hz), 132.2 (d, J = 1.68 Hz), 132.1 (d, J = 4.47 Hz), 131.7, 129.1, 128.9, 128.7, 128.4 (d, J = 11.00 Hz), 128.4, 128.0, 127.7, 127.0, 126.7 (d, J = 5.76 Hz), 124.6 (d, J = 13.40 Hz), 119.8 (d, J = 13.03 Hz), 116.2 (d, J = 177.19 Hz), 63.2 (d, J = 6.93 Hz), 16.4 (d, J = 6.39 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ 9.92; IR (film) 3056, 2982, 1243, 1022, 963, 748 cm^{-1}; HRMS (EI) m/z calcd for $C_{26}H_{21}O_3P$ 412.1228, found 412.1230.

3aa: R_f = 0.3 (EtOAc/hexane 1/5); pale green oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, J = 6.36, 1H), 8.02 (d, J = 16.08, 1H), 4.28−4.15 (m, 2H), 2.74−2.45 (m, 8H), 1.34−1.17 (m, 15H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 155.7, 152.4 (d, J = 10.91 Hz), 136.9 (d, J = 6.53 Hz), 135.6 (d, J = 16.16 Hz), 128.2 (d, J = 176.81 Hz), 125.0 (d, J = 12.05 Hz), 124.5 (d, J = 10.00 Hz), 124.2, 115.2 (d, J = 11.23 Hz), 112.9, 63.0 (d, J = 6.52 Hz), 25.4 (d, J = 5.23 Hz), 24.1, 21.0, 19.3, 16.5 (d, J = 6.00 Hz), 14.5, 14.2, 12.5, 11.7; ^{31}P NMR (121 MHz, $CDCl_3$) δ 8.62; IR (film) 2971, 2876, 1732, 1632, 1470, 1278, 1029, 947, 789 cm^{-1}; HRMS (EI) m/z calcd for $C_{21}H_{27}O_3P$ 390.1596, found 390.1596.

3,4-Bis(3-methylphenyl)-1-phenyl-1H-2,1-benzoxaphosphorin 1-oxide ***(5b):*** R_f = 0.4 (EtOAc/hexane 1/1); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96−7.91 (m, 2H), 7.63−7.49 (m, 4H), 7.44 (tt, J = 7.4, 1.3 Hz, 1H), 7.35−7.25 (m, 2H), 7.18−7.15 (m, 2H), 7.10 (s, 1H), 7.08−7.05 (m, 2H), 6.98−6.95 (m, 3H), 2.33 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.9 (d, J = 11.0 Hz), 138.9 (d, J = 5.2 Hz), 137.1, 136.0, 134.6 (d, J = 5.1 Hz), 132.9 (d, J = 2.9 Hz), 132.45 (d, J = 2.5 Hz), 132.41, 132.3, 132.1, 131.0, 130.2 (d, J = 12.3 Hz), 129.6, 129.5, 129.2, 129.0, 128.5 (d, J = 1.4 Hz), 127.5 (d, J = 14.5 Hz), 127.3, 126.9 (d, J = 9.6 Hz), 126.3, 123.1 (d, J = 129.6 Hz), 119.0 (d, J = 11.0 Hz), 21.4, 21.3; ^{31}P NMR (161 MHz, $CDCl_3$) δ 24.38; IR (film) 3054, 2920, 1590, 1240, 1065 cm^{-1}; HRMS (EI) m/z calcd for $C_{28}H_{23}O_2P$ 422.1436, found 422.1437.

3,4-Bis(4-methylphenyl)-1-phenyl-1H-2,1-benzoxaphosphorin 1-oxide ***(5c):*** R_f = 0.3 (EtOAc/hexane 1/1); yellow solid, mp 219−221 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95−7.90 (m, 2H), 7.62−7.48 (m, 4H), 7.43 (t, J = 7.7 Hz, 1H), 7.33−7.29 (m, 1H), 7.21−7.13 (m, 6H), 7.05 (dd, J = 8.4, 4.8 Hz, 1H), 6.92 (d, J = 8.1, 2H), 2.40 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.9 (d, J = 10.9 Hz), 139.1 (d, J = 5.5 Hz), 138.4, 137.3, 133.1, 132.9 (d, J = 2.7 Hz), 132.4 (d, J = 2.6 Hz), 132.3 (d, J = 11.0 Hz), 131.9 (d, J = 5.0 Hz), 131.4, 131.0, 130.2 (d, J = 12.3 Hz), 129.7, 129.6 (d, J = 11.5 Hz), 128.6 (d, J = 71.0 Hz), 128.5 (d, J = 13.9 Hz), 127.4 (d, J = 14.3 Hz), 126.7 (d, J = 9.6 Hz), 123.1 (d, J = 129.7 Hz), 118.4 (d, J = 11.0 Hz), 21.3, 21.2; ^{31}P NMR (161 MHz, $CDCl_3$) δ 24.39; IR (film) 3054, 2920, 1590, 1240, 1060, 738 cm^{-1}; HRMS (EI) m/z calcd for $C_{28}H_{23}O_2P$ 422.1436, found 422.1436.

3,4-Bis(4-methoxyphenyl)-1-phenyl-1H-2,1-benzoxaphosphorin 1-oxide ***(5d):*** R_f = 0.3 (EtOAc/hexane 1/1); yellow solid, mp 58−60 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95−7.90 (m, 2H), 7.63−7.49 (m, 4H), 7.43 (t, J = 7.7 Hz, 1H), 7.33−7.28 (m, 1H), 7.19 (app d, J = 8.9 Hz, 4H), 7.07 (dd, J = 8.04, 4.82 Hz, 1H), 6.94 (d, J = 8.7 Hz, 2H), 6.65 (app d, J = 9.0, 2H), 3.85 (s, 3H), 3.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 159.1, 146.8 (d, J = 11.0 Hz), 139.3 (d, J = 5.4 Hz), 132.9 (d, J = 2.7 Hz), 132.7, 132.4 (d, J = 4.5 Hz), 132.3 (d, J = 11.1 Hz), 130.5, 130.22 (d, J = 144.9 Hz), 130.21 (d, J = 12.4 Hz), 128.5 (d, J = 13.9 Hz), 128.4 (d, J = 6.0 Hz), 127.3 (d, J = 5.3 Hz), 127.2 (d, J = 15.0 Hz), 126.6 (d, J = 9.8 Hz), 123.0 (d, J = 129.9 Hz), 117.5 (d, J = 11.0 Hz), 114.5, 113.0, 55.3, 55.2; ^{31}P NMR (161 MHz, $CDCl_3$) δ 24.45; IR (film) 3055, 2959, 1605, 1245, 1175, 1028, 741 cm^{-1}; HRMS (EI) m/z calcd for $C_{28}H_{23}O_4P$ 454.1334, found 454.1333.

3,4-Bis(3-chlorophenyl)-1-phenyl-1H-2,1-benzoxaphosphorin 1-oxide ***(5e):*** R_f = 0.4 (EtOAc/hexane 1/1); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95−7.90 (m, 2H), 7.67−7.47 (m, 5H), 7.41−7.33 (m, 3H), 7.31 (d, J = 1.5 Hz, 2H), 7.18−7.15 (m, 2H), 7.07−7.01 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.8 (d, J = 10.9 Hz), 137.7 (d, J = 5.1 Hz), 137.5, 136.1 (d, J = 5.1 Hz), 133.9, 133.3 (d, J = 2.8 Hz), 132.7 (d, J = 2.5 Hz), 132.4 (d, J = 11.1 Hz), 131.4, 130.5 (d, J = 12.5 Hz), 130.1, 129.8, 129.0 (d, J = 7.2 Hz), 128.9, 128.8, 128.7, 128.6, 128.4, 128.2, 128.1, 127.3, 126.7 (d, J = 9.4 Hz), 123.3 (d, J = 128.9 Hz). 118.9 (d, J = 11.2 Hz); ^{31}P NMR (161 MHz, $CDCl_3$) δ 24.54; IR (film) 3059, 1592, 1470, 1237, 1064, 733 cm^{-1}; HRMS (EI) m/z calcd for $C_{26}H_{17}Cl_2O_2P$ 462.0343, found 462.0345.

3,4-Bis(4-chlorophenyl)-1-phenyl-1H-2,1-benzoxaphosphorin 1-oxide ***(5f):*** R_f = 0.4 (EtOAc/hexane 1/1); yellow solid, mp 58−60 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95−7.89 (m, 2H), 7.66−7.45 (m, 5H), 7.40−7.34 (m, 3H), 7.21 (d, J = 8.2 Hz, 2H), 7.17−7.11 (m, 4H), 7.01 (dd, J = 7.9, 4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.0 (d, J = 11.0 Hz), 138.0 (d, J = 5.2 Hz), 134.7, 134.2 (d, J = 8.5 Hz), 133.2 (d, J = 2.8 Hz), 133.0, 132.9, 132.7 (d, J = 2.4 Hz), 132.4 (d, J = 11.2 Hz), 130.5, 130.4, 130.2, 129.4, 128.7 (d, J = 14.2 Hz), 128.1 (overlapped), 128.0 (d, J = 11.4 Hz), 126.6 (d, J = 9.5 Hz), 123.3 (d, J = 129.7 Hz), 118.5 (d, J = 11.3 Hz); ^{31}P NMR (161 MHz, $CDCl_3$) δ 24.52; IR (film) 3057, 1590, 1236, 1091, 728 cm^{-1}; HRMS (EI) m/z calcd for $C_{26}H_{17}Cl_2O_2P$ 462.0343, found 462.0345.

3,4-Bis(3-bromophenyl)-1-phenyl-1H-2,1-benzoxaphosphorin 1-oxide ***(5g):*** R_f = 0.45 (EtOAc/hexane 1/1); pale yellow solid, mp 115−117 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95−7.89 (m, 2H), 7.67−7.52 (m, 5H), 7.50−7.46 (m, 3H), 7.40−7.36 (m, 1H), 7.33−7.26 (m, 2H), 7.21 (d, J = 7.6 Hz, 1H), 7.08−6.97 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.7 (d, J = 10.9 Hz), 137.8, 137.7 (d, J = 5.1 Hz), 136.3 (d, J = 5.1 Hz), 134.3, 133.3 (d, J = 2.8 Hz), 132.7 (d, J = 2.6 Hz), 132.4 (d, J = 11.2 Hz), 131.9 (d, J = 4.5 Hz), 131.4, 130.6 130.4 (d, J = 12.6 Hz), 130.3, 130.1, 129.2, 128.7 (d, J = 14.0 Hz), 128.2 (d, J = 14.3 Hz), 127.8, 126.7 (d, J = 9.5 Hz), 123.3 (d, J = 129.1 Hz), 161.9, 118.8 (d, J = 11.1 Hz); ^{31}P NMR (161 MHz, $CDCl_3$) δ 24.60; IR (film) 3058, 2925, 1590, 1242, 1062, 747 cm^{-1}; HRMS (EI) m/z calcd for $C_{26}H_{17}Br_2O_2P$ 549.9333, found 549.9333.

3,4-Bis(4-bromophenyl)-1-phenyl-1H-2,1-benzoxaphosphorin 1-oxide ***(5h):*** R_f = 0.5 (EtOAc/hexane 1/1); pale yellow solid, mp 169−171 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94−7.89 (m, 2H), 7.66−7.51 (m, 6H), 7.47 (tt, J = 7.7, 1.2 Hz, 1H), 7.39−7.34 (m, 1H), 7.28 (app d, J = 8.7 Hz, 2H), 7.15 (d, J = 8.2 Hz, 2H), 7.09 (app d, J = 8.7 Hz, 2H), 7.01 (dd, J = 8.0, 4.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.0 (d, J = 11.1 Hz), 137.9 (d, J = 5.2 Hz), 134.8, 133.4 (d, J = 5.1 Hz), 133.24, 133.20, 132.7 (d, J = 2.3 Hz), 132.5, 132.4, 131.0, 130.6, 130.4 (d, J = 12.5 Hz), 130.2, 128.6 (d, J = 14.1 Hz), 128.0 (d, J = 14.3 Hz), 126.6 (d, J = 9.4 Hz), 123.3 (d, J = 129.7 Hz), 123.1, 122.4, 118.6 (d, J = 11.5 Hz); ^{31}P NMR (161 MHz, $CDCl_3$) δ 24.49; IR (film) 3057, 1586, 1484, 1236, 1072, 950, 740 cm^{-1}; HRMS (EI) m/z calcd for $C_{26}H_{17}Br_2O_2P$ 549.9333, found 549.9333.

1-Phenyl-3,4-diethyl-1H-2,1-benzoxaphosphorin 1-oxide ***(5i):*** R_f = 0.3 (EtOAc/hexane 1/1); colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82−7.77 (m, 2H), 7.59−7.51 (m, 2H), 7.50−7.44 (m, 3H), 7.30−7.26 (m, 1H), 2.60−2.34 (m, 4H), 1.23−1.16 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.8 (d, J = 11.5 Hz), 137.4 (d, J = 5.3 Hz), 132.7 (d, J = 2.8 Hz), 132.6 (d, J = 2.3 Hz), 132.2 (d, J = 10.9 Hz), 130.6 (d, J = 12.4 Hz), 130.3 (d, J = 144.2 Hz), 128.4 (d, J = 13.8 Hz), 126.7 (d, J = 14.5 Hz), 123.6 (d, J = 129.8 Hz), 123.5 (d, J = 10.0 Hz), 114.4 (d, J = 11.2 Hz), 25.5 (d, J = 4.8 Hz), 20.9, 14.2, 11.6; ^{31}P NMR (161 MHz, $CDCl_3$) δ 10.34; IR (film) 3059, 1633, 1469, 1240, 1130, 1046 cm^{-1}; HRMS (EI) m/z calcd for $C_{18}H_{19}O_2P$ 298.1123, found 298.1123.

1-Phenyl-3.4-dibutyl-1H-2,1-benzoxaphosphorin 1-oxide ***(5j):*** R_f = 0.4 (EtOAc/hexane 1/1); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81−7.75 (m, 2H), 7.59−7.55 (m, 2H), 7.51−7.44 (m, 4H), 7.31−7.26 (m, 1H), 2.60−2.40 (m, 4H), 1.64−1.50 (m, 4H), 1.49−1.28 (m, 4H), 0.98 (t, J = 7.2, 3H), 0.89 (t, J = 7.34, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.9 (d, J = 11.1 Hz), 137.7 (d, J = 5.2 Hz), 132.7 (d, J = 2.9 Hz), 132.6 (d, J = 2.2 Hz), 132.1 (d, J = 10.9 Hz), 130.6 (d, J = 12.4 Hz), 130.4 (d, J = 143.8 Hz), 128.4 (d, J = 13.7 Hz), 126.6 (d, J = 14.6 Hz), 123.58 (d, J = 9.9 Hz), 123.57 (d, J = 129.8 Hz), 113.7 (d, J = 11.4 Hz), 32.0 (d, J = 4.7 Hz), 31.7, 29.0, 27.5, 22.9, 22.4, 14.0, 13.9; ^{31}P NMR (161 MHz, $CDCl_3$) δ 23.94; IR (film) 2957, 2930, 1630, 1467, 1242, 1130, 745 cm^{-1}; HRMS (EI) m/z calcd for $C_{22}H_{27}O_2P$ 354.1749, found 354.1750.

8-Methyl-1-(2-methylphenyl)-3,4-diphenyl-1H-2,1-benzoxaphosphorin 1-oxide ***(5k):*** R_f = 0.4 (EtOAc/hexane 1/1); white solid, mp 53−55 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28−8.22 (m, 1H),

7.49 (tt, J = 7.5, 1.4 Hz, 1H), 7.42−7.30 (m, 5H), 7.25−7.21 (m, 3H), 7.20−7.18 (m, 2H), 7.13−7.06 (m, 4H), 6.88 (dd, J = 8.1, 4.5 Hz, 1H), 2.29 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.3 (d, J = 11.8 Hz), 141.8 (d, J = 10.3 Hz), 140.6 (d, J = 11.7 Hz), 139.5 (d, J = 5.5 Hz), 136.7, 134.8 (d, J = 5.1 Hz), 134.5 (d, J = 11.5 Hz), 133.0 (d, J = 2.5 Hz), 132.2 (d, J = 2.0 Hz), 131.8, 131.5 (d, J = 12.7 Hz), 130.2 (d, J = 12.7 Hz), 130.0 (d, J = 142.1 Hz), 129.0, 128.8, 128.3, 127.7, 127.5, 125.8 (d, J = 14.0 Hz), 125.2 (d, J = 9.5 Hz), 161.8 (d, J = 126.2 Hz), 118.8 (d, J = 11.4 Hz), 21.3 (d, J = 6.0 Hz), 20.6 (d, J = 4.5 Hz); ^{31}P NMR (161 MHz, $CDCl_3$) δ 21.68; IR (film) 3054, 2979, 1619, 1455, 1234, 1093 cm^{-1}; HRMS (EI) m/z calcd for $C_{28}H_{23}O_2P$ 422.1436, found 422.1436.

*8-Methyl-1-(2-methylphenyl)-3,4-diethyl-1H-2,1-benzoxaphosphorin 1-oxide (**5l**):* R_f = 0.4 (EtOAc/hexane 1/1); pale yellow solid, mp 117−119 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18−8.12 (m, 1H), 7.49−7.43 (m, 2H), 7.38−7.33 (m, 2H), 7.18 (t, J = 6.5 Hz, 1H), 7.06 (dd, J = 7.6, 4.3 Hz, 1H), 2.66−2.45 (m, 4H), 2.18 (s, 3H), 2.01 (s, 3H), 1.18 (td, J = 7.5, 3.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.1 (d, J = 11.8 Hz), 141.7 (d, J = 10.2 Hz), 140.7 (d, J = 11.8 Hz), 138.0 (d, J = 5.4 Hz), 134.3 (d, J = 11.5 Hz), 132.7 (d, J = 2.7 Hz), 132.3 (d, J = 2.1 Hz), 131.3 (d, J = 12.6 Hz), 130.2 (d, J = 141.49 Hz), 129.2 (d, J = 12.9 Hz), 125.7 (d, J = 13.9 Hz), 122.4 (d, J = 126.6 Hz), 161.6 (d, J = 9.7 Hz), 113.9 (d, J = 11.7 Hz), 25.5 (d, J = 4.8 Hz), 21.4 (d, J = 6.0 Hz), 21.2, 20.5 (d, J = 4.5 Hz), 14.4, 11.7; ^{31}P NMR (161 MHz, $CDCl_3$) δ 20.94; IR (film) 2969, 1640, 1456, 1232, 1054, 734 cm^{-1}; HRMS (EI) m/z calcd for $C_{20}H_{23}O_2P$ 326.1436, found 326.1438.

*6-Methoxy-1-(4-methoxyphenyl)-3,4-diphenyl-1H-2,1-benzoxaphosphorin 1-oxide (**5m**):* R_f = 0.40 (EtOAc/hexane 1/1); pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, J 12.7, 8.7 Hz, 2H), 7.54 (dd, J = 13.7, 8.4 Hz, 1H), 7.39−7.32 (m, 3H), 7.28−7.26 (m, 2H), 7.23−7.20 (m, 2H), 7.15−7.07 (m, 3H), 7.00 (dd, J = 8.7, 2.8 Hz, 2H), 6.87 (dt, J = 8.4, 2.3 Hz, 1H), 6.54−6.52 (m, 1H), 3.86 (s, 3H), 3.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3 (d, J = 3.1 Hz), 162.7 (d, J = 2.9 Hz), 147.5 (d, J = 10.9 Hz), 140.9 (d, J = 6.5 Hz), 136.2, 134.9 (d, J = 5.1 Hz), 134.3 (d, J = 12.6 Hz), 132.3 (d, J = 13.7 Hz), 131.6, 129.1, 128.9, 128.4, 127.8, 127.5, 121.8 (d, J = 152.8 Hz), 118.9 (d, J = 10.8 Hz), 115.6 (d, J = 136.0 Hz), 114.1 (d, J = 15.2 Hz), 113.4 (d, J = 15.2 Hz), 112.3 (d, J = 10.5 Hz), 55.4, 55.2; ^{31}P NMR (161 MHz, $CDCl_3$) δ 26.00; IR (film) 3656, 3452, 3056, 3021, 2966, 2937, 1572, 1555, 1304, 1227, 1165, 1125 cm^{-1}; HRMS (EI) m/z calcd for $C_{28}H_{23}O_4P$ 454.1334, found 454.1337.

*6-Methoxy-1-(4-methoxyphenyl)-3,4-diethyl-1H-2,1-benzoxaphosphorin 1-oxide (**5n**):* R_f = 0.45 (EtOAc/hexane 1/1); colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (dd, J = 12.6, 8.8 Hz, 2H), 7.42 (dd, J = 13.8, 8.4 Hz, 1H), 6.98−6.93 (m, 3H), 6.82 (dt, J = 8.4, 2.3 Hz, 1H), 3.86 (s, 3H), 2.60−2.41 (m, 4H), 1.21 (t, J = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 1630 (d, J = 3.0 Hz), 162.9 (d, J = 2.8 Hz), 151.4 (d, J = 11.3 Hz), 139.6 (d, J = 6.5 Hz), 134.0 (d, J = 12.4 Hz), 132.5 (d, J = 13.4 Hz), 122.1 (d, J = 151.7 Hz), 116.1 (d, J = 136.4 Hz), 114.0 (d, J = 11.0 Hz), 113.9 (d, J = 14.9 Hz), 111.9 (d, J = 15.3 Hz), 109.4 (d, J = 10.8 Hz), 55.3 (d, J = 2.5 Hz), 21.6 (d, J = 4.9), 21.0; ^{31}P NMR (161 MHz, $CDCl_3$) δ 25.12; 26.00; IR (film) 2967, 2936, 2875, 2839, 1597, 1305, 1257, 1226, 1129 cm^{-1}; HRMS (EI) m/z calcd for $C_{20}H_{23}O_4P$ 358.1334, found 358.1331.

*6-Chloro-1-(4-chlorophenyl)-3,4-bis(4-methoxyphenyl)-1H-2,1-benzoxaphosphorin 1-oxide (**5o**):* R_f = 0.55 (EtOAc/hexane 1/1); pale yellow solid, mp 197−199 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87−7.81 (m, 2H), 7.52−7.44 (m, 3H), 7.29 (td, J = 8.1, 2.1 Hz, 1H), 7.17−7.14 (m, 4H), 7.05 (dd, J = 4.1, 4.8 Hz, 1H), 6.95 (app d, J = 8.7, 2H), 6.67−6.63 (m, 2H), 3.87 (s, 3H), 3.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 159.4, 147.9 (d, J = 11.2 Hz), 141.2 (d, J = 6.0 Hz), 139.9 (d, J = 3.6 Hz), 139.4 (d, J = 3.3 Hz), 133.7 (d, J = 11.8 Hz), 132.6, 131.5 (d, J = 13.2 Hz), 130.6, 129.1 (d, J = 14.8 Hz), 129.0 (d, J = 3.7 Hz), 127.54 (d, J = 15.7 Hz), 127.50 (d, J = 4.1 Hz), 126.6 (d, J = 3.6 Hz), 126.6 (d, J = 10.2 Hz), 120.8 (d, J = 132.5 Hz), 116.8 (d, J = 10.6 Hz), 114.7, 113.1, 55.3, 55.2; ^{31}P NMR (161 MHz, $CDCl_3$) δ 22.77; IR (film) 3052, 2958, 1606, 1252, 1060, 765 cm^{-1}; HRMS (EI) m/z calcd for $C_{28}H_{21}Cl_2O_4P$ 522.0555, found 522.0557.

*6-Chloro-1-(4-chlorophenyl)-3,4-diethyl-1H-2,1-benzoxaphosphorin 1-oxide (**5p**):* R_f = 0.55 (EtOAc/hexane 1/1); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73−7.68 (m, 2H), 7.48−7.45 (m, 3H), 7.39 (dd, J = 13.9, 8.1 Hz, 1H), 7.29−7.26 (m, 1H), 2.63−2.44 (m, 4H), 1.21 (t, J = 7.3 Hz, 3H), 1.18 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.1 (d, J = 11.1 Hz), 139.7 (d, J = 3.6 Hz), 139.5 (d, J = 3.4 Hz), 139.3 (d, J = 6.2 Hz), 133.5 (d, J = 11.8 Hz), 131.9 (d, J = 13.2 Hz), 128.9 (d, J = 14.6 Hz), 127.6, 127.0 (d, J = 15.2 Hz), 123.8 (d, J = 10.6 Hz), 161.5 (d, J = 132.6 Hz), 113.9 (d, J = 11.1 Hz), 25.6 (d, J = 4.8 Hz), 20.8, 14.1, 11.5; ^{31}P NMR (161 MHz, $CDCl_3$) δ 22.30; IR (film) 3054, 2970, 1583, 1242, 1087, 798 cm^{-1} HRMS (EI) m/z calcd for $C_{18}H_{17}Cl_2O_2P$ 366.0343, found 366.0345.

*1-(Naphthalen-1-yl)-3,4-bis(p-methoxyphenyl)-1H-naphtho[1,2-c][1,2]oxaphosphinine 1-oxide (**5q**):* R_f = 0.45 (EtOAc/hexane 1/1); yellow solid, mp 148−150 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43−8.38 (m, 2H), 8.24 (d, J = 8.0 Hz, 1H), 8.05 (d, J = 8.2 Hz, 1H), 7.87−7.85 (m, 2H), 7.73 (d, J = 8.1 Hz, 1H), 7.58 (td, J = 7.6, 2.9 Hz, 1H), 7.44−7.40 (m, 2H), 7.35 (d, J = 7.8 Hz, 1H), 7.32−7.23 (m, 4H), 7.11 (d, J = 8.7 Hz, 2H), 6.98 (d, J = 8.4 Hz, 2H), 6.56 (d, J = 8.8 Hz, 2H), 3.86 (s, 3H), 3.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 159.2, 147.7 (d, J = 12.1 Hz), 139.7 (d, J = 5.0 Hz), 134.7 (d, J = 12.0 Hz), 134.1 (d, J = 3.1 Hz), 133.8 (d, J = 10.9 Hz), 133.1, 133.0, 132.8, 132.4 (d, J = 11.3 Hz), 132.1 (d, J = 11.2 Hz), 130.6, 129.2, 129.0, 128.8, 128.4, 127.9, 127.8, 127.5, 127.0 (d, J = 5.6 Hz), 126.4 (d, J = 18.1 Hz), 126.1 (d, J = 7.3 Hz), 125.6 (d, J = 5.6 Hz), 124.7, 124.6 (d, J = 2.6 Hz), 117.8 (d, J = 127.4 Hz), 117.5 (d, J = 12.2 Hz), 114.6, 112.9, 55.3, 55.1; ^{31}P NMR (161 MHz, $CDCl_3$) δ 23.77; IR (film) 3055, 2957, 1606, 1508, 1250, 1026, 806 cm^{-1}; HRMS (EI) m/z calcd for $C_{36}H_{27}O_4P$ 554.1647, found 554.1650.

*1-(2,4,6-Trimethylphenyl)-3,4-diethyl-1H-2,1-benzoxaphosphorin 1-oxide (**5r**):* R_f = 0.5 (EtOAc/hexane 1/1); pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54−7.47 (m, 2H), 7.35−7.30 (m, 1H), 7.24−7.19 (m, 1H), 6.92 (s, 1H), 6.91 (s, 1H), 2.70−2.49 (m, 4H), 2.36 (s, 6H), 2.31 (s, 3H), 1.23 (t, J = 7.9 Hz, 3H), 1.21 (t, J = 7.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.1 (d, J = 11.2 Hz), 145.1 (d, J = 11.9 Hz), 142.9 (d, J = 2.8 Hz), 136.2 (d, J = 5.0 Hz), 131.9 (d, J = 2.3 Hz), 130.9 (d, J = 13.6 Hz), 129.1 (d, J = 13.8 Hz), 126.5 (d, J = 15.0 Hz), 126.3 (d, J = 127.1 Hz), 123.4 (d, J = 9.5 Hz), 122.0 (d, J = 142.3 Hz), 114.1 (d, J = 11.7 Hz), 25.7 (d, J = 4.6 Hz), 22.9 (d, J = 3.6 Hz), 21.1, 20.9, 14.4, 11.7; ^{31}P NMR (161 MHz, $CDCl_3$) δ 23.97; IR (film) 2969, 1629, 1469, 1230, 1046, 746 cm^{-1}; HRMS (EI) m/z calcd for $C_{21}H_{25}O_2P$ 340.1592, found 340.1594.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, tables, and figures giving general comments, additional data for optimization of reaction conditions, and ^{1}H and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

Dedicated to Professor Hong-SeoK Kim, Kyungpook National University, on the occasion of his 60th birthday.

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