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Ring Opening of Triflates Derived from Benzophospholan-3-one Oxides by Aryl Grignard Reagents as a Route to 2-Ethynylphenyl(diaryl)phosphine Oxides

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ABSTRACT: A new simple method for the synthesis of 2-ethynylphenyl(diaryl)phosphine oxides via ring opening of benzophosphol-3-yl triflates has been developed. This process occurs via nucleophilic attack of a Grignard reagent at the phosphorus center, which results in ring opening and cleavage of a leaving group. The reaction proceeds under mild conditions and, within 15–60 min, leads to a library of previously unavailable 2-ethynylphenylphosphine oxides in yields up to 98%.



INTRODUCTION

Compounds possessing an ethynyl fragment became an attractive pattern in modern organic chemistry.¹ The growing importance of the chemistry of carbon-carbon triple bonds is due to their unique and diverse chemical reactivity and remarkable synthetic potential as they can be used as precursors for many classes of compounds including alkanes, alkenes, aldehydes, and carboxylic acids on both laboratory and industrial scales.^{1,2} Recently, ethynyl compounds have been intensively explored in catalytic reactions mediated by different metals (gold,³ copper,⁴ palladium,⁵ rhodium,⁶ and others⁷), providing various cyclic products. Moreover, ethynyl compounds have a wide range of applications in the synthesis of biologically active compounds and have been broadly exploited in drug discovery and development.8 Furthermore, an alkyne functionality is frequently used in medicine⁹ and chemical biology¹⁰ as a "click" probe to label or identify molecular targets and to assess target engagement. The "click-type" reactions of ethynyl compounds have also been exploited to synthesize π -conjugated macromolecules for organic electronics¹¹ and other materials.¹² On the other hand, ethynyl compounds themselves, especially those possessing expanded π -systems, have been involved in the preparation of organic structures for photo-optical purposes and others.¹³ All mentioned applications of alkynes benefit from the rapid development of the synthetic routes, enabling the incorporation of an ethynyl unit into the structure of nearly any organic molecule. The most explored methods here are Sonogashira coupling,¹⁴ copper-free Sonogashira reactions,¹⁵ and alkynylation reaction.¹⁶

In the field of organophosphorus chemistry, (ethynyl)phosphine oxides were employed in the preparations of socalled "smart" polymers¹⁷ but also as the starting materials for metal-catalyzed coupling,¹⁸ cyclization,¹⁹ cycloaddition,²⁰ and radical addition/cycloaddition.²¹ Another class of organophosphorus-possessing C-C triple bond compounds mentioned in the literature is *p*-ethynylphenylphosphine oxides. Those compounds have found several applications in the construction of star-shaped fluorescent molecules,²² microporous organic polymers (MOPs),²³ nanostructured carbon materials,²⁴ and triazole precursors.²⁵ Their *ortho* analogues with phosphorus at a lower oxidation state are typically used for the construction of the benzophosphole skeleton.²⁶ The access to those derivatives was achieved via a reaction of olithiotolane with chlorophosphine (Scheme 1A).^{26e,27} A different route to these derivatives was completed through Sonogashira coupling.²⁸ In 2020, Duan et al. showed that methyl(phenyl)phosphinic chloride in a reaction with lithium o-phenylethynylbenzene had provided o-phenylethynylphosphine oxide, which is immediately transformed into the corresponding benzophosphole oxide (Scheme 1B).²⁹ Another compound possessing an ethynyl moiety in the ortho position was obtained via [2 + 2 + 2] cyclization (Scheme 1, C).³⁰ To the best of our knowledge, the phosphine oxides possessing a terminal ethynyl moiety in the ortho position are unknown. The closest known analogues are derivatives of (oethynylphenyl)phosphonic acid synthesized by Ding³¹ and later Peng.32

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Scheme 1. Examples of the Synthesis of 2-Ethynylphenylphosphine Derivatives





RESULTS AND DISCUSSION

Herein, we want to present a new route to 2-ethynylphenyl-(diaryl)phosphine oxides via unprecedented ring opening of triflates derived from benzophospholan-3-one oxides.

We began our study with the preparation of a set of triflates 5 and 6 from benzophospholan-3-one oxides 3 and benzophospholan-3-one sulfide 4a (Scheme 2, path d). Benzophospholan-3-one oxides 3 and sulfide 4a, which were starting materials for triflates 5 and 6a, were prepared in a two-step procedure, utilizing Ullman type coupling of phosphine oxide 1 followed by cyclization in the presence of LDA (Scheme 2, paths a and b). The preparation of benzophosphole sulfide 4a was achieved via chemoselective reduction of P=O in 3 followed by oxidation of the phosphorus center with sulfur (Scheme 2, path c).

Our primary synthetic goal was to investigate the reactivity of triflates 5 and 6a toward aryl Grignard reagents in order to

Scheme 2. Synthetic Route to Triflates 5 and 6

prepare 3-arylbenzophosphole oxides 7 according to the reaction depicted in Scheme 3.

Scheme 3. Predicted Outcome of the Reaction of 5a with Aryl Grignard Reagents



In order to check the reactivity of triflates toward the Grignard reagent, the model triflate 5a was reacted with *p*-tolylmagnesium bromide (Table 1). To our surprise, instead of

Table 1. Optimization of Reaction Conditions in a Reaction of 5a and p-TolMgBr⁴



^{*a*}Reaction conditions: **5a** (0.13 mmol), ArMgBr (0.195 mmol), THF (2 mL). ^{*b*}Isolated yields. ^{*c*}Starting material **5a** and 1-phenylbenzophospholan-3-one oxide (**3a**) were present in the crude reaction mixture. ^{*d*}Reaction was carried out for 30 min.

the expected 1-phenyl-3-(p-tolyl)benzophosphole oxide (7a), we have observed compound 8a (as the major product), which, in most cases, remained in the mixture with diphosphorus compound 9 (Table 1, entries 1–5). We





Figure 1. Molecular structure of **9**; ellipsoids 30%, hydrogen atoms have been omitted for clarity (except H35). Important bond distances (Å), angles (deg) for **9**: P1–O1 1.488(2), P2–O2 1.482(2), C20–C21 1.202(4), C34–C35 1.205(6), C35–H35 0.950(2), O1–P1–C1 111.41(14), O1–P1–C8 113.03(15), O1–P1–C14 113.89(15), C20–C21–P2 168.8(3), O2–P2–C22 113.86(16), O2–P2–C28 115.37(15), C33–C34–C35 176.0(3).

realized that the aryl Grignard reagent caused the ring opening of the starting triflate 5a, which resulted in the formation of phosphine oxide 8a bearing a 2-ethynylphenyl substituent. Therefore, we decided to focus on the selective transformation of triflates into phosphine oxides 8 possessing a terminal ethynyl group in the *ortho* position, which gives an opportunity for further functionalization.

First, we screened the influence of the temperature on the reaction of triflate 5a with *p*-TolMgBr (Table 1, entries 1–4). Preliminary attempts showed that the selectivity of the reaction is significantly affected by temperature. When the reaction of 5a was carried out at -78 °C, a mixture of products was observed in the crude reaction mixture, and the conversion of 5a was not complete (Table 1, entry 1). The mixture consisted of 8a, 9, and unreacted 5a and was accompanied by 1phenylbenzophospholan-3-one oxide (3a). We were able to isolate major product 8a along with diphosphorus compound 9 in 36% and 29% yields, respectively. Under these conditions, selectivity was low, and a relatively high amount of 9 was formed. The structure of compound 9 was confirmed by X-ray analysis (Figure 1). It turned out that compound 9 possesses an alkyne moiety directly connected with the phosphorus atom.

Further attempts have revealed that the full conversion of 5a can be achieved by increasing the temperature (Table 1, entry 2). Additionally, the amount of 8a has significantly increased at -25 °C, 0 °C, and rt to 71, 65, and 76% isolated yields, respectively (Table 1, entries 2-4). However, some amounts of 9 have still been found in the reaction mixture and were isolated in 7-17% yields. To optimize the conditions, we decided to maintain the temperature of the reaction at 0 °C. A further study has shown that the change in the 5a/p-TolMgBr ratio strongly affected the outcome of the reaction (Table 1, entries 4-6). In the case where 5a was reacted with 2.5 equiv of the Grignard reagent, desired 8a was formed as a sole product isolated in 83% yield (Table 1, entry 6). Finally, the optimal reaction conditions were established by reducing the amount of *p*-TolMgBr and extending the reaction time (Table 1, entry 7). In this case, the complete conversion of 5a to 8a was observed, and 8a was isolated with the highest yield (98%).

In the next stage, the reactivity of triflate **5a** toward a set of aryl Grignard reagents was checked under the optimized reaction conditions (Table 2). In general, triflate **5a** was





^{*a*}Reaction conditions: **5a** (0.13 mmol), ArMgBr (0.195 mmol), THF (2 mL). ^{*b*}Isolated yields of product. ^{*c*}Numbers in parentheses indicate yields according to ³¹P NMR. ^{*d*}Reaction was carried out on a 0.6 mmol scale. ^{*e*}Reaction was carried out with *o*-TolMgCl. ^{*f*}Formation of a small amount of ketone **3a** was observed but not isolated. ^{*g*}Additionally, 7% of **3a** was isolated.

tolerant toward different substitution patterns in the aryl ring of the Grignard reagent used. In most cases, products 8a-kwere obtained in good to very good yields. In the case of tolyl Grignard reagents, there was no difference between the reactivity of the *p*- and *m*-tolyl Grignard reagent, and both led to the formation of 8a and 8b in 98% and 84% yields, respectively. In sharp contrast to these reactions, the analogous reaction with *o*-TolMgCl was much less selective and resulted in a mixture of 8c and ketone 3a. In this case, product 8c was formed with the lowest yield (38%). Noteworthy, the reaction with *p*-TolMgBr on a higher scale (0.6 mmol) has also provided desired product 8a in a high yield (91%).

At the same time, the reactivity of triflate **5a** toward the Grignard reagent possessing electro-donating substituents (anisylmagnesium bromides) was not greatly dependent on the position of the methoxyl group in the phenyl ring. The reactions of compound **5a** with any isomer (*o*-, *m*-, *p*-) of anisylmagnesium bromide provided products **8d**-f with 89–98% yields. Another Grignard reagent with an electron-donating substituent, p-Me₂N-C₆H₄MgBr, in a reaction with **5a** has provided a mixture of **8k** and **3a**, which was enriched in **8k**. In this case, **8k** and **3a** were isolated in 60 and 7% yields, respectively.

Interestingly, even Grignard reagents possessing halogen atoms in the *para* position in the phenyl ring formed the desired products with a very high selectivity; however, isolated yields of **8i** and **8j** were slightly lower (82% yields for both reagents). In turn, a reaction of **5a** under the same conditions with bulky 9-phenantrylmagnesium bromide has led to product **8h** in 70% yield. Small amounts of other unidentified compounds were also observed but not isolated.

The results achieved for 5a (Table 2) have prompted us to further investigate the selectivity of this process by changing the substituents in compound 5. The obtained results are presented in Table 3. To our delight, once again, we were able to isolate the expected 2-ethynylphenyl(diaryl)phosphine oxides 10-12 in very good yields. In the case of compounds with electron-donating substituents in benzophosphole rings 5b and 5d, a reaction with PhMgBr afforded 10d and 12d in high yields -91 and 82%, respectively. Similar results were obtained when compound 5c possessing a chlorine substituent was subjected to the reaction with PhMgBr. Product 11d was successfully isolated in a 73% yield. Moreover, the reactions of 5b with other Grignard reagents (p-TolMgBr, p-AnMgBr, p- $Cl-C_6H_4MgBr$) provided 10–11a,e,i as the major products in the crude reaction mixture. Therefore, we assume that the studied reaction is tolerant toward differently substituted aryl Grignard reagents. Unfortunately, the isolation step was less successful in comparison to products formed in reactions with PhMgBr (10d, 11d, 12d). In these cases, we noted lower isolated yields in the range of 58-66%. Faster isolation of 10-12 (higher polarity of the eluent, short chromatography column) resulted in higher yields and moderate purity. In opposite, when compounds were eluted slower (lower polarity of eluent, longer chromatography column), higher purity was noted with a significant reduction of yield. For instance, when isolating 10a in a lower polarity solvent and a higher polarity solvent, we observed 38% and 66% yields, respectively. It seems that a terminal acetylene moiety can interact with acidic silica gel, which causes a decrease in yield. Unfortunately, some loss during isolation was also observed for products 10k, 11k, and 12k possessing an amino moiety. Even the addition of triethylamine to the eluent during the chromatography column was not beneficial, and all of these products were isolated in a moderate yield, 60-70%.

To verify the influence of the P = X center on the reaction course, sulfide **6a** derived from 1-phenylbenzophosphole sulfide **(4a)** was subjected to the reaction with PhMgBr. In contrast to phosphine oxide **5a**, phosphine sulfide **6a** turned



Table 3. Reactivity of Substituted Benzophosphole Oxides 5b-d with Aryl Grignard Reagents^{*a,b,c*}



^{*a*}Reaction conditions: **5a** (0.13 mmol), ArMgBr (0.195 mmol), THF (2 mL). ^{*b*}Isolated yields of product. ^{*c*}Numbers in parentheses indicate yields according to ³¹P NMR. ^{*d*}Formation of a small amount of ketone **3a** was observed but not isolated.

out to be unreactive under the developed conditions, and **6a** has been recovered in 72% yield (Scheme 4).

Scheme 4. Reactivity of 6a toward PhMgBr



In the last part of the study, we subjected triflate 5a to the reactions with different organometallic nucleophiles (Scheme 5). In the case of the reaction with phenyllithium, the selectivity of the reaction toward the formation of 8d has lowered in comparison to the use of PhMgBr. Compound 8d was still the main product but has remained in the mixture with other unidentified products. Finally, we were able to isolate 8d in a 21% yield. In turn, the reaction with the alkyl Grignard reagent has led to similar reactivity as it was observed for aryl Grignard reagents. As the result of the reaction of 5a with EtMgBr, ethyl(2-ethynylphenyl)phenylphosphine oxide (13) was observed as a major product in the reaction mixture and isolated in 58% yield.

Scheme 5. Reactivity of 5a toward Different Organometallic Nucleophiles



^a Reaction conditions: **5a** (0.108 mmol), RX (0.164 mmol), THF (2 mL). ^a Isolated yields of product (%). ^c Numbers in parentheses indicate yields according to ³¹P NMR (%).

A plausible mechanism for the formation of 2ethynylphenyl(diaryl)phosphine oxides is depicted in Scheme 6 (eq 1). This includes the attack of an aryl Grignard reagent (II) on the phosphorus atom in triflate I, which, in turn, causes the opening of the five-membered ring and the formation of a triple bond in the *ortho* position to the phosphorus center. The consequence of the ring opening is the cleavage of the leaving group (⁻OTf), resulting in the formation of 2-ethynylphenyl-(diaryl)phosphine oxide (III).

In eq 2, a plausible mechanism of the subsequent reaction of phosphine oxide III, leading to compound V, is presented. The deprotonation of the formed phosphine oxide III by an aryl Grignard reagent leads to the formation of an anion IV, which competes with the Grignard reagent in a reaction with another molecule of I. The attack of anion IV leads to an analogous ring opening of I as it was observed for the Grignard reagent. In accordance with eq 1, the formation of a triple bond in the *ortho* position in compound V is observed. As a consequence, product V with an alkyne-phosphorus bond is formed.

CONCLUSION

In summary, we developed a facile method for the synthesis of 2-ethynylphenyl(diaryl)phosphine oxides from readily available reagents under mild conditions and in a short time. It is the first example of the preparation of arylphosphine oxides possessing a terminal ethynyl moiety in the *ortho* position in a phenyl ring. The mechanism for the formation of both 2-ethynylphenyl(diaryl)phosphine oxides **8** and diphosphorus compound **9** has been proposed. The scope of the method for diverse substitution patterns in a structure of a Grignard

reagent, benzophosphole core, and phosphorus atom has been investigated. The application of the method for the higherscale preparations has been confirmed. The study of reactivity of 2-ethynylphenyl(diaryl)phosphine oxides and compound **9** is underway in our laboratory.

EXPERIMENTAL SECTION

All reactions were performed under an argon atmosphere using Schlenk techniques. Only dry solvents were used, and glassware was heated under a vacuum prior use. All chemicals were used as received unless noted otherwise. Solvents for chromatography and crystallization were distilled once before use, and the solvents for extraction were used as received. THF and toluene were distilled from sodium/ benzophenone ketyl under argon. DCM was dried using P_4O_{10} and distilled before use.

¹H NMR, ³¹P{¹H} NMR, and ¹³C{¹H} NMR spectra were recorded on a Bruker Advance 500 spectrometer at an ambient temperature in CDCl₃ unless otherwise noted. Chemical shifts (δ) are reported in ppm from tetramethylsilane with the solvent as an internal indicator (CDCl₃ 7.27 ppm for ¹H and 77 ppm for ¹³C). Structural assignments were made with additional information from DEPT experiments. Mass spectra were recorded on Shimadzu GC-MS QP2010S in electron ionization (EI). Melting points were determined on a Büchi Melting Point M-560 in a capillary tube and were uncorrected. HPLC-HRMS was performed on a Shimazu HRMS ESI-IT-TOF using a reverse-phase stationary phase with water/ MeCN (65:35) as an eluent, electrospray ionization (ESI), and an IT-TOF detector. Elementary analyses were performed on a Perkin Elmer CHN 2400. Thin-layer chromatography (TLC) was performed with precoated silica gel plates and visualized by UV light or KMnO4 solution or iodide on silica gel. The reaction mixtures were purified by column chromatography over silica gel (60-240 mesh).

Single crystals for 9 were obtained by dissolving 35 mg of 9 (an oil from chromatography column) in about 1 mL of AcOEt. Then 24 h later at 25 $^{\circ}$ C, colorless crystals appeared. Obtained crystals were isolated and dried for 24 h in rt.

The X-ray intensity data for **9** were collected on a diffractometer IPDS2T equipped with a STOE image plate detector system using a microfocus X-ray source providing K α radiation by high-grade multilayer X-ray mirror optics for a Mo ($\lambda = 0.71073$ Å) wavelength. The measurement was carried out at 120 K. The structure of the compounds was solved by direct methods and refined against F^2 with the Shelxs-2008 and Shelxl-2008 programs³³ run under WinGX.³⁴ Non-hydrogen atoms were refined with anisotropic displacement parameters. The isotropic displacement parameters of all hydrogens were fixed to 1.2 U_{eq} for CH and CH₂ (1.5 times for methyl groups).

Scheme 6. Plausible Mechanism of the Formation of Products 8a and 9



The crystallographic data for the structure of **9** reported in this work have been deposited in the Cambridge Crystallograic Data Centre (CCDC 2094907).

The starting compounds were prepared according to reported methods: phenyl(methyl)phosphine oxide,³⁵ methyl 2-iodobenzoate,³⁶ methyl 2-iodo-6-methylbenzoate,³⁷ methyl 2-iodo-5-chlorobenzoate,³⁸ 2-iodo-4-methoxybenzoic acid,³⁹ methyl 2-iodo-4methoxybenzoate.⁴⁰

Syntheses of 2-Methoxycarbonylphenylphosphine Oxides 2 Were Performed According to a Reported Procedure (General Procedure A).³⁵ (2-Methoxycarbonylphenyl)(methyl)-phenylphosphine Oxide (2a).³⁵ Methyl(phenyl)phosphine oxide (1.248 g, 8.91 mmol) was reacted according to a reported procedure³⁵ with methyl 2-iodobenzoate (2.567 g, 9.7 mmol) to afford 2a (66%, 1.61 g, 5.9 mmol). ¹H NMR (500 MHz, CDCl₃): δ 8.33–8.53 (m, 1H), 7.87–7.89 (m, 1H), 7.68–7.71 (m, 1H), 7.56–7.63 (m, 3H), 7.42–7.49 (m, 1H), 7.68–7.71 (m, 2H), 3.54 (s, 3H), 2.22 (d, *J*_{P-H} = 13.87 Hz, 3H). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 167.0 (d, *J*_{P-H} = 2.7 Hz, C), 134.5 (d, *J*_{P-H} = 107.2 Hz, C), 134.3 (d, *J*_{P-H} = 7.3 Hz, CH), 133.8 (d, *J*_{P-H} = 92.6 Hz, C), 133.6 (d, *J*_{P-H} = 6.4 Hz, CH), 131.7 (s), 131.6 (s), 131.2 (d, *J*_{P-H} = 2.7 Hz, CH), 130.2 (d, *J*_{P-H} = 8.2 Hz, CH), 129.8 (d, *J*_{P-H} = 10.0 Hz, CH), 128.2 (d, *J*_{P-H} = 11.8 Hz, CH), 52.7 (s, H₃CO), 16.3 (d, *J*_{P-H} = 77.2 Hz, CH₃). ³¹P{¹H} NMR (202 MHz, CDCl₃): δ 33.45 (s).

[(2-Methoxycarbonyl)-6-methylphenyl]methylphenylphosphine Oxide (2b). Methyl(phenyl)phosphine oxide (2.2 g, 15.7 mmol) was reacted according to a reported procedure³⁵ with methyl 2-iodo-6methylbenzoate (4.77 g, 17.4 mmol) to afford 2b as a brown solid (65%, 2.96 g, 10.2 mmol). Mp: 73.4–74.2 °C. $R_f = 0.34$ (30:5:1 CHCl₃/AcOEt/MeOH). ¹H NMR (500 MHz, CDCl₃): δ 7.66–7.70 (m, 2H), 7.49–7.53 (m, 1H), 7.43–7.56 (m, 3H), 7.36–7.40 (m, 1H), 7.27–7.31 (m, 1H), 3.69 (s, 3H), 2.35 (s, 3H), 2.17 (d, $J_{P-H} =$ 13.40 Hz, 3H). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 170.2 (d, J_{C-P} = 4.5 Hz, C), 142.6 (d, J_{C-P} = 9.1 Hz, C), 139.1 (d, J_{C-P} = 7.3 Hz, C), 135.1 (d, J_{C-P} = 103.5 Hz, C), 133.6 (d, J_{P-C} = 10.0 Hz, CH), 131.6 (d, $J_{C-P} = 2.7$ Hz, CH), 131.2 (d, $J_{C-P} = 1.8$ Hz, CH), 130.1 (d, J_{C-P} = 10.9 Hz, 2CH), 129.9 (d, J_{C-P} = 94.5 Hz, C), 128.6 (d, J_{C-P} = 11.8 Hz, 2CH), 126.1 (d, J_{C-P} = 9.1 Hz, CH), 52.6 (s, H₃CO), 22.7 (d, $J_{C-P} = 4.5 \text{ Hz}, \text{ CH}_3$, 16.6 (d, $J_{C-P} = 74.6 \text{ Hz}, \text{ CH}_3$). ³¹P{¹H} NMR (202 MHz, CDCl₃): δ 32.57 (s). GC-MS (EI) m/z: 274 (29) (M-CH₃+H)⁺, 273 (100) (M-CH₃)⁺, 256 (14), 213 (10), 195 (27), 179 (8), 178 (8), 167 (13), 166 (15), 165 (48), 152 (16), 139 (24), 137 (11), 121 (12), 109 (12), 107 (9), 91 (29), 90 (18), 89 (46), 79 (14), 78 (60), 77 (99), 74 (16). HRMS (ESI/Q-TOF) m/z: [M + Na]⁺calcd for C₁₆H₁₇O₃PNa, 311.0808; found, 311.0802.

[(2-Methoxycarbonyl)-5-chlorophenyl]methylphenylphosphine Oxide (2c). Methyl(phenyl)phosphine oxide (2.41 g, 17.2 mmol) was reacted according to a reported procedure³⁵ with methyl 5-chloro-2iodo-benzoate (5.16 g, 17.4 mmol) to afford 2c as a brown solid (52%, 2.74 g, 8.9 mmol). Mp: 111–112 °C. $R_f = 0.38 (30:5:1 \text{ CHCl}_3/10^{-1})$ AcOEt/MeOH). ¹H NMR (500 MHz, CDCl₃): δ 8.43-8.46 (m, 1H), 7.85-7.88 (m, 1H), 7.58-7.63 (m, 3H), 7.47-7.51 (m, 1H), 7.41–7.45 (m, 2H), 3.56 (s, 3H), 2.25 (d, J_{P-H} = 14.19 Hz, 3H). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 166.1 (d, J_{C-P} = 1.8 Hz, C), 139.0 (d, J_{C-P} = 13.6 Hz, C), 136.7 (d, J_{C-P} = 89.0 Hz, C), 134.7 (d, $J_{C-P} = 7.3$ Hz, CH), 134.1 (d, $J_{C-P} = 108.1$ Hz, C), 131.8 (d, $J_{C-P} =$ 9.1 Hz, CH), 131.7 (d, J_{C-P} = 1.8 Hz, CH), 131.5 (d, J_{C-P} = 2.7 Hz, CH), 129.9 (d, $J_{C-P} = 10.0$ Hz, CH), 128.3 (d, $J_{C-P} = 12.7$ Hz, CH), 52.4 (s, CH₃), 16.0 (d, $J_{C-P} = 78.1$ Hz, CH₃). ³¹P{¹H} NMR (202 MHz, CDCl₃): δ 32.44 (s). GC–MS (EI) m/z: 295 (22), 294 (7), 293(72) (M-CH₃)⁺, 263 (6), 165 (9), 163 (11), 154 (11), 153 (8), 152 (18), 151 (17), 139 (28), 138 (17), 126 (10). HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ calcd for $C_{15}H_{14}ClO_3PNa$, 331.0261; found, 331.0270.

[(2-Methoxycarbonyl)-4-methoxyphenyl]methylphenylphosphine Oxide (2d). Methyl(phenyl)phosphine oxide (2.27 g, 16.2 mmol) was reacted according to a reported procedure³⁵ with methyl 2-iodo-4-methoxy-benzoate (5.25 g, 17.98 mmol) to afford 2d as a yellowish solid (55%, 2.71 g, 8.91 mmol). Mp: 115.9–116.5 °C. $R_f = 0.28$ (30:5:1 CHCl₃/AcOEt/MeOH). ¹H NMR (500 MHz, CDCl₃): δ 8.26–8.31 (m, 1H), 7.58–7.62 (m, 2H), 7.42–7.49 (m, 1H), 7.39–7.41 (m, 3H), 7.17–7.20 (m, 1H), 3.89 (s, 3H), 3.54 (s, 3H), 2.19 (d, J_{P-H} = 14.2 Hz, 3H). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 166.8 (d, J_{C-P} = 1.8 Hz, C), 162.0 (d, J_{C-P} = 1.8 Hz, C), 136.4 (d, J_{C-P} = 9.1 Hz, CH), 135.3 (d, J_{C-P} = 7.3 Hz, C), 135.1 (d, J_{C-P} = 106.3 Hz, C), 131.1 (d, J_{C-P} = 2.7 Hz, CH), 129.8 (d, J_{C-P} = 100.0 Hz, 2CH), 128.2 (d, J_{C-P} = 12.7 Hz, 2CH), 124.8 (d, J_{C-P} = 100.0 Hz, C), 116.5 (d, J_{C-P} = 2.7 Hz, CH), 116.4 (d, J_{C-P} = 5.5 Hz, CH), 55.6 (s, CH₃), 52.2 (s, CH₃), 16.6 (d, J_{C-P} = 78.1 Hz, CH₃). ³¹P{¹H} NMR (202 MHz, CDCl₃): δ 32.55 (s). GC–MS (EI): *m/z* 304 (2) (M)⁺, 290 (18), 289 (100) (M-CH₃)⁺, 273 (13), 257 (16), 227 (13), 211 (13), 139 (31), 121 (11), 107 (10), 91 (14), 77 (50). HRMS (ESI/Q-TOF) *m/z*: [M + H]⁺ calcd for C₁₆H₁₇O₄P, 305.0937; found, 305.0929.

Synthesis of Benzophospholan-3-one Oxides 3 (General Procedure B).⁴¹ To a Schlenk tube (100 mL) equipped with a magnetic stirrer and an argon inlet phosphine was added oxide 2 (2.0 mmol) in anhydrous THF (15 mL), and the mixture was cooled to -78 °C with a dry ice/acetone bath. Then, LDA (2.5 mL, 5.0 mmol, 2 M solution) was added, and the mixture was stirred at the same temperature for 30 min. After that time, the ice bath was removed. The reaction mixture was stirred at rt overnight and then quenched by the addition of a saturated NH₄Cl solution (5 mL) and extracted with CHCl₃ (5 \times 10 mL). The collected organic phases were dried over Na₂SO₄, the solid was filtered off, and the filtrate was evaporated under reduced pressure. The crude residue was checked using NMR techniques. Then, the crude mixture was dissolved in DCM (30 mL), solution of HCl (1 M, 10 mL) was added, and the mixture was vigorously stirred for 30 min. Then the acidic water phase was removed in a separating funnel, the organic phase was returned to the flask, and another portion of HCl (1 M, 10 mL) was added. The mixture was once again vigorously stirred for 30 min, and after that time, the acidic water phase was separated. The organic phase was washed with water (10 mL) and dried over Na₂SO₄. The solid was filtered off, and the filtrate was evaporated under reduced pressure. The residue was purified by short (5 cm) column chromatography on silica gel using CHCl₃/acetone (2:1 v/v) or CHCl₃/EtOAc/MeOH (30:5:1 v/v/v) as an eluent.

Benzophospholan-3-one Oxide (**3a**).²⁹ Compound **2a** (0.55 g, 2.0 mmol) was reacted according to general procedure B to afford **3a** (55%, 0.266 g, 1.1 mmol). ¹H NMR (500 MHz, CDCl₃): δ 8.03–8.07 (m, 1H), 7.85–7.90 (m, 1H), 7.75–7.83 (m, 2H), 7.52–7.60 (m, 3H), 7.44–7.48 (m, 2H), 3.12–3.31 (m, 2H). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 194.3 (d, $J_{C-P} = 12.7$ Hz, C), 141.5 (d, $J_{C-P} = 91.7$ Hz, C), 141.3 (d, $J_{C-P} = 12.7$ Hz, C), 141.5 (d, $J_{C-P} = 91.7$ Hz, C), 141.3 (d, $J_{C-P} = 12.7$ Hz, C), 135.9 (d, $J_{C-P} = 10.9$ Hz, CH), 133.6 (d, $J_{C-P} = 2.7$ Hz, CH), 132.5 (d, $J_{C-P} = 2.7$ Hz, CH), 130.8 (d, $J_{C-P} = 10.9$ Hz, CH), 128.9 (d, $J_{C-P} = 10.9$ Hz, CH), 124.6 (d, $J_{C-P} = 10.9$ Hz, CH), 40.1 (d, $J_{C-P} = 71.8$ Hz, CH₂). ³¹P{¹H} NMR (202 MHz, CDCl₃): δ 29.92 (s).

7-Methylbenzophospholan-3-one Oxide (3b). Compound 2b (0.577 g, 2.0 mmol) was reacted according to general procedure B to afford 3b as a beige solid (55%, 0.28 g, 1.1 mmol). Mp: 165-166 °C (dec.). $R_f = 0.66$ (2:1 CHCl₃/acetone). ¹H NMR (500 MHz, CDCl₃): δ 7.78-7.7.92 (m, 1H), 7.64-7.68 (m, 1H), 7.53-7.63 (m, 4H), 7.46–7.58 (m, 2H), 3.09–3.32 (m, 2H), 2.43 (s, 3H). ${}^{13}C{}^{1}H{}$ NMR (125 MHz, CDCl₃): δ 194.6 (d, J_{C-P} = 13.6 Hz, C), 142.0 (d, $J_{C-P} = 5.5 \text{ Hz}, \text{ C}$), 141.8 (d, $J_{C-P} = 12.7 \text{ Hz}, \text{ C}$), 139.7 (d, $J_{C-P} = 90.8$ Hz, C), 137.1 (d, J_{C-P} = 9.1 Hz, CH), 133.9 (d, J_{C-P} = 1.8 Hz, CH), 132.4 (d, J_{C-P} = 3.6 Hz, CH), 130.9 (d, J_{C-P} = 103.5 Hz, C), 130.6 (d, $J_{\rm C-P}$ = 10.9 Hz, CH), 129.0 (d, $J_{\rm C-P}$ = 12.7 Hz, CH), 122.2 (d, $J_{\rm C-P}$ = 11.8 Hz, CH), 40.5 (d, J_{C-P} = 71.5 Hz, CH₂), 19.4 (d, J_{C-P} = 4.5 Hz, CH₃). ³¹P{¹H} NMR (202 MHz, CDCl₃): δ 30.36 (s). GC–MS (EI) *m/z*: 258 (7), 257 (13), 256 (63) (M)⁺, 255 (37), 236 (8), 213 (24), 179 (9), 166 (28), 165 (42), 151 (10), 150 (12), 137 (14), 121 (12), 106 (29). HRMS (ESI/Q-TOF) m/z: calcd for $C_{15}H_{13}O_2P$ [M + Na]⁺, 279.0545; found, 279.0553.

6-Chlorobenzophospholan-3-one Oxide (3c). Compound 2c (0.617 g, 2.0 mmol) was reacted according to general procedure B to afford 3c as an orange oil (55%, 0.3 g, 1.1 mmol). $R_f = 0.36$ (30:5:1

CHCl₃/AcOEt/MeOH). ¹H NMR (500 MHz, CDCl₃): δ 7.99–8.01 (m, 1H), 7.81–7.84 (m, 1H), 7.72–7.74 (m, 1H), 7.58–7.62 (m, 3H), 7.49–7.52 (m, 2H), 3.16–3.36 (m, 2H). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 192.9 (d, $J_{C-P} = 12.7$ Hz, C), 143.5 (d, $J_{C-P} = 108.1$ Hz, C), 143.1 (d, $J_{C-P} = 33.6$ Hz, C), 139.5 (d, $J_{C-P} = 12.7$ Hz, C), 134.2 (d, $J_{C-P} = 2.7$ Hz, CH), 132.9 (d, $J_{C-P} = 3.6$ Hz, CH), 130.7 (d, $J_{C-P} = 10.9$ Hz, CH), 130.1 (d, $J_{C-P} = 106.3$ Hz, C), 129.3 (d, $J_{C-P} = 6.4$ Hz, CH), 129.2 (d, $J_{C-P} = 14.5$ Hz, CH), 126.1 (d, $J_{C-P} = 11.8$ Hz, CH), 40.2 (d, $J_{C-P} = 71.8$ Hz, CH₂). ³¹P{¹H} NMR (202 MHz, CDCl₃): δ 32.55 (s). GC–MS (EI) *m*/*z*: 278 (14), 277 (7), 276 (49) (M)⁺, 235 (14), 234 (14), 233 (57). HRMS (ESI/Q-TOF) *m*/*z*: calcd for C₁₄H₁₀ClO₂P [M + H]⁺, 277.0180; found, 277.0180.

5-Methoxybenzophospholan-3-one Oxide (3d). Compound 2d (0.609 g, 2.0 mmol) was reacted according to general procedure B to afford 3d as a brown oil (59%, 0.32 g, 1.18 mmol). $R_f = 0.72$ (2:1 CHCl₃/acetone). ¹H NMR (500 MHz, CDCl₃): δ 7.74–7.78 (m, 1H), 7.52–7.59 (m, 3H), 7.44–7.47 (m, 3H), 7.32–7.35 (m, 1H), 3.93 (m, 3H), 3.11–3.32 (m, 2H). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 194.3 (d, $J_{C-P} = 12.7$ Hz, C), 164.2 (d, $J_{C-P} = 2.7$ Hz, C), 144.0 (d, $J_{C-P} = 14.5$ Hz, C), 133.2 (d, $J_{C-P} = 97.2$ Hz, C), 132.4 (d, $J_{C-P} = 3.6$ Hz, CH), 133.2 (d, $J_{C-P} = 107.2$ Hz, C), 130.7 (d, $J_{C-P} = 10.7$ Hz, 2CH), 130.6 (d, $J_{C-P} = 7.4$ Hz, CH), 129.0 (d, $J_{C-P} = 12.9$ Hz, 2CH), 124.7 (d, $J_{C-P} = 7.4$ Hz, CH), 106.5 (d, $J_{C-P} = 12.6$ Hz, CH), 55.9 (s, OCH₃), 40.8 (d, $J_{C-P} = 71.8$ Hz, CH₂). ³¹P{¹H} NMR (202 MHz, CDCl₃): δ 28.92 (s). GC–MS (EI) m/z: 273 (24), 272 (100) (M)⁺, 271 (17), 256 (12), 244 (21), 229 (49), 210 (12), 208 (15), 195 (18), 193 (19), 183 (10), 179 (31), 165 (21), 153 (12), 152 (29), 148 (13), 139 (21), 137 (11), 120 (43), 107 (24), 91 (36), 89 (14). HRMS (ESI/Q-TOF) m/z: calcd for C₁₅H₁₃O₃P [M + H]⁺, 273.0675; found, 273.0681.

Synthesis of Benzophospholan-3-one Sulfide (4a, General Procedure C). To a Schlenk tube (100 mL) equipped with a magnetic stirrer and an argon inlet was added phosphine oxide 3a (0.528 g, 2.18 mmol) in anhydrous toluene (20 mL). Then, HSiCl₃ (2.2 mL, 21.8 mmol) was added, and the mixture was stirred at rt for 18 h. The crude reaction mixture was checked using the ³¹P{¹H} NMR technique. Then, sulfur (21.8 mmol) was added, and the reaction mixture was stirred at rt for 8 h. Then, the reaction mixture was quenched by the addition of saturated NH₄Cl solution (5 mL) and extracted with CHCl₃ (5 × 10 mL). The collected organic phases were dried over Na₂SO₄, the solid was filtered off, and the filtrate was evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel using hexane/*i*-PrOH (10:1 v/v) as an eluent.

Benzophospholan-3-one Sulfide (4a). Compound 3a (0.48 g, 2.0 mmol) was reacted according to general procedure C to afford 4 as a brownish oil (67%, 0.346 g, 1.34 mmol). $R_f = 0.44$ (10:1 hexane/i-PrOH). ¹H NMR (500 MHz, CDCl₃): δ 8.03–8.07 (m, 1H), 7.83– 7.91 (m, 2H), 7.74-7.78 (m, 1H), 7.65-7.70 (m, 2H), 7.52-7.53 (m, 1H), 7.44–7.48 (m, 2H), 3.35–3.47 (m, 2H). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (125 MHz, CDCl₃): δ 195.3 (d, J_{C-P} = 9.1 Hz, C), 143.4 (d, J_{C-P} = 76.3 Hz, C), 139.6 (d, J_{C-P} = 10.9 Hz, C), 136.4 (d, J_{C-P} = 11.8 Hz, CH), 132.9 (d, $J_{C-P} = 2.7$ Hz, CH), 132.1 (d, $J_{C-P} = 3.6$ Hz, CH), 131.2 (d, J_{C-P} = 81.8 Hz, C), 130.8 (d, J_{C-P} = 11.8 Hz, 2CH), 129.4 (d, J_{C-P} = 7.3 Hz, CH), 128.9 (d, J_{C-P} = 12.7 Hz, 2CH), 128.3 (d, J_{C-P} = 19.9 Hz, C), 124.8 (d, J_{C-P} = 10.9 Hz, CH), 45.8 (d, J_{C-P} = 57.2 Hz, CH₂). ³¹P{¹H} NMR (202 MHz, CDCl₃): δ 32.02 (s). GC-MS (EI) m/z: 260 (7), 259 (58) (M)⁺, 258 (100), 226 (15), 184 (10), 185 (33), 165 (24), 153 (11), 152 (31), 151 (7), 150 (12), 149 (98), 139 (21), 136 (10), 134 (12), 121 (36), 120 (12), 118 (11), 109 (44), 108 (24), 107 (67), 95 (13), 91 (29), 90 (15), 89 (20), 81 (19), 78 (20). Anal. Calcd for C₁₄H₁₁OPS: C, 65.10; H, 4.29. Found: C, 64.90; H, 4.10.

Synthesis of Triflates 5 and 6a (General Procedure D). To a Schlenk tube (50 mL) equipped with a magnetic stirrer and an argon inlet was added phosphine oxide 3 (0.3 mmol) or sulfide 4a (0.3 mmol) in anhydrous DCM (8 mL), and the mixture was cooled to -78 °C with a dry ice/acetone bath. DIPEA (78.4 μ L, 0.45 mmol) was added dropwise. Then, Tf₂O (61 μ L, 0.36 mmol) was added dropwise with vigorous stirring. The reaction mixture was stirred at

 $-78~^{\rm C}$ for 30 min. The crude reaction mixture was checked using the $^{31}{\rm P}\{^{1}{\rm H}\}$ NMR technique. Then, the reaction mixture was quenched by the addition of 1 M HCl solution (5 mL) and extracted with CHCl₃ (5 \times 10 mL). The collected organic phases were dried over Na₂SO₄, the solid was filtered off, and the filtrate was evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel using CHCl₃/acetone (2:1 v/v) as an eluent.

1-Oxido-1-phenyl-1H-phosphindol-3-yl Trifluoromethanesulfonate (5a). Compound 3a (0.073 g, 0.3 mmol) was reacted according to general procedure D to afford 5a as an orange solid (75%, 0.084 g, 0.225 mmol). Mp: 120.1–121.1 °C. $R_f = 0.76$ (2:1 CHCl₃/acetone). ¹H NMR (500 MHz, CDCl₃): δ 7.68–7.75 (m, 3H), 7.62–7.66 (m, 1H), 7.56-7.61 (m, 1H), 7.52-7.57 (m, 2H), 7.46-7.50 (m, 2H), 6.31 (d, $J_{H-P} = 14.82$ Hz, 1H). ¹³C{¹H} NMR (125 MHz, CDCl₂): δ 156.7 (d, J_{C-P} = 34.5 Hz, C), 135.8 (d, J_{C-P} = 19.1 Hz, C), 133.4 (d, $J_{C-P} = 1.8$ Hz, CH), 133.1 (d, $J_{C-P} = 2.7$ Hz, CH), 132.2 (d, $J_{C-P} =$ 104.5 Hz, C), 131.5 (d, J_{C-P} = 10.9 Hz, CH), 130.8 (d, J_{C-P} = 10.9 Hz, 2CH), 129.5 (d, J_{C-P} = 8.2 Hz, CH), 129.1 (d, J_{C-P} = 12.7 Hz, 2CH), 127.5 (d, J_{C-P} = 108.1 Hz, C), 121.0 (d, J_{C-P} = 10.9 Hz, CH), 118.5 (q, J_{C-P} = 321.5 Hz, CF₃), 108.9 (d, J_{C-P} = 95.4 Hz, CH). ³¹P{¹H} NMR (202 MHz, CDCl₃): δ 32.12 (s). ¹⁹F NMR (470 MHz, $CDCl_3$: δ -72.96 (s). GC-MS (EI) m/z: 374 (5) (M)⁺, 240 (23), 194 (44), 183 (11), 179 (6), 178 (31), 177 (6), 166 (16), 165 (44), 152 (11), 151 (7), 107 (15), 89 (12), 77 (17), 69 (100). HRMS (ESI/Q-TOF) m/z: calcd for $C_{15}H_{10}F_3O_4PS$ [M + H]⁺, 375.0062; found, 375.0053.

1-Oxido-1-phenyl-1H-7-methylphosphindol-3-yl Trifluoromethanesulfonate (5b). Compound 3b (0.077 g, 0.3 mmol) was reacted according to general procedure D to afford 5b as a yellow solid (55%, 0.064 g, 0.165 mmol). Mp: 125–126.5 °C. R_f = 0.68 (2:1 CHCl₃/acetone). ¹H NMR (500 MHz, CDCl₃): δ 7.73–7.77 (m, 2H), 7.58-7.61 (m, 1H), 7.47-7.53 (m, 3H), 7.35-7.37 (m, 1H), 7.27–7.29 (m, 2H), 6.25 (d, J_{H-P} = 15.13 Hz, 1H), 2.37 (s, 3H). $^{13}\text{C}\{^{1}\text{H}\}$ NMR (125 MHz, CDCl₃): δ 156.8 (d, $J_{\text{C-P}}$ = 34.5 Hz, C), 142.2 (d, J_{C-P} = 8.2 Hz, C), 135.8 (d, J_{C-P} = 19.1 Hz, C), 133.5 (d, $J_{\rm C-P}=$ 2.7 Hz, CH), 133.1 (d, $J_{\rm C-P}=$ 10.0 Hz, CH), 132.9 (d, $J_{\rm C-P}=$ 2.7 Hz, CH), 130.8 (d, J_{C-P} = 10.9 Hz, 2CH), 130.3 (d, J_{C-P} = 103.5 Hz, C), 129.2 (d, J_{C-P} = 13.6 Hz, 2CH), 127.3 (d, J_{C-P} = 106.3 Hz, C), 118.5 (q, $J_{C-P} = 321.5$ Hz, CF₃), 118.48 (d, $J_{C-P} = 10.9$ Hz, CH), 108.9 (d, $J_{C-P} = 95.4$ Hz, CH), 19.4 (s, CH₃). ³¹P{¹H} NMR (202 MHz, CDCl₃): δ 32.47 (s). ¹⁹F NMR (470 MHz, CDCl₃): δ -72.98 (s). GC-MS (EI) m/z: 388 (9) (M)⁺, 255 (9), 208 (33), 192 (18), 178 (16), 165 (26), 89 (13), 77 (19). HRMS (ESI/Q-TOF) m/z: calcd for $C_{16}H_{12}O_4F_3PS [M + H]^+$, 389.0219; found, 389.0213.

1-Oxido-1-phenyl-1H-6-chlorophosphindol-3-yl Trifluoromethanesulfonate (5c). Compound 3c (0.083 g, 0.3 mmol) was reacted according to general procedure D to afford 5c as an orange oil (60%, 0.074 g, 0.18 mmol). $R_f = 0.75$ (2:1 CHCl₃/acetone). ¹H NMR (500 MHz, CDCl₃): δ 7.71–7.75 (m, 2H), 7.58–7.65 (m, 3H), 7.45–7.52 (m, 3H), 6.31 (d, J_{H-P} = 15.29 Hz, 1H). ¹³C{¹H} NMR (125 MHz, $CDCl_3$): δ 156.2 (d, J_{C-P} = 33.6 Hz, C), 138.4 (d, J_{C-P} = 14.3 Hz, C), 134.6 (d, J_{C-P} = 100.8 Hz, C), 133.9 (d, J_{C-P} = 19.1 Hz, C), 133.4 (d, $J_{C-P} = 2.7$ Hz, CH), 133.3 (d, $J_{C-P} = 1.8$ Hz, CH), 130.8 (d, $J_{C-P} =$ 10.9 Hz, 2CH), 128.9 (d, J_{C-P} = 10.0 Hz, CH), 128.4 (d, J_{C-P} = 13.6 Hz, 2CH), 126.7 (d, J_{C-P} = 108.9 Hz, C), 122.2 (d, J_{C-P} = 11.8 Hz, CH), 118.5 (q, J_{C-P} = 320.6 Hz, CF₃), 109.9 (d, J_{C-P} = 98.6 Hz, CH). ³¹P{¹H} NMR (202 MHz, CDCl₃): δ 31.06 (s). ¹⁹F NMR (470 MHz, $CDCl_3$): δ -72.83 (s). GC-MS (EI) m/z: 411 (3) 410 (10), 409 (5), 408 (28) (M)⁺, 277 (16), 276 (16), 275 (51), 259 (22), 232 (11), 229 (30), 229 (20), 228 (100), 214 (30), 213 (14), 212 (92), 211 (11), 199 (22), 196 (22), 193 (36), 183 (13), 176 (16), 166 (16), 165 (75), 164 (14), 151 (24), 140 (11), 107 (21), 105 (28), 89 (12). HRMS (ESI/Q-TOF) m/z: calcd for $C_{15}H_9ClF_3O_4PS$ [M + H]⁺, 408.9673; found, 408.9681.

1-Oxido-1-phenyl-1H-5-methoxyphosphindol-3-yl Trifluoromethanesulfonate (5d). Compound 3c (0.082 g, 0.3 mmol) was reacted according to general procedure D to afford 5d as an orange oil (58%, 0.07 g, 0.174 mmol). R_f = 0.65 (2:1 CHCl₃/acetone). ¹H NMR (500 MHz, CDCl₃): δ 7.68–7.72 (m, 2H), 7.55–7.62 (m, 2H), 7.44–7.48 (m, 2H), 7.03–7.04 (m, 1H), 6.97–7.00 (m, 1H), 6.30 (d, $J_{H-P} = 14.66$ Hz, 1H), 3.90 (s, 3H). $^{13}C{^{1}H}$ NMR (125 MHz, CDCl₃): δ 164.0 ($J_{P-C} = 1.8$ Hz, C), 155.9 (d, $J_{P-C} = 33.6$ Hz, C), 138.2 (d, $J_{P-C} = 20.9$ Hz, C), 132.9 (d, $J_{P-C} = 2.7$ Hz, CH), 131.1 (d, $J_{P-C} = 10.0$ Hz, CH), 130.8 (d, $J_{P-C} = 11.8$ Hz, 2CH), 129.1 (d, $J_{P-C} = 13.6$ Hz, CC), 118.6 (q, $J_{P-C} = 10.8.9$ Hz, C), 122.7 (d, $J_{P-C} = 11.8$ Hz, CH), 110.5 (d, $J_{P-C} = 320.6$ Hz, CF₃), 115.5 (d, $J_{P-C} = 12.7$ Hz, CH), 110.5 (d, $J_{P-C} = 94.5$ Hz, CH), 108.0 (d, $J_{P-C} = 11.8$ Hz, CH), 55.8 (s, CH₃). $^{31}P{^{1}H}$ NMR (202 MHz, CDCl₃): δ 30.95 (s). ^{19}F NMR (470 MHz, CDCl₃): $\delta - 72.89$ (s). GC–MS (EI) *m/z*: 405 (2), 404 (11) (M)⁺, 282 (13), 281 (33), 273 (11), 272 (62) (M-SO₂CF₃), 271 (57), 256 (72), 240 (20), 229 (24), 224 (71) 223 (18), 209 (38), 208 (94), 207 (100), 196 (15), 195 (25), 179 (49), 165 (29), 152 (34), 151 (18), 148 (18), 139 (24), 137 (18), 120 (36), 106 (24), 91 (47), 89 (19). HRMS (ESI/Q-TOF) *m/z*: calcd for C₁₆H₁₂O₅F₃PS [M + H]⁺, 405.0168; found, 405.0165.

1-Sulfido-1-phenyl-1H-phosphindol-3-yl Trifluoromethanesulfonate (6a). Compound 4a (0.077 g, 0.3 mmol) was reacted according to general procedure D to afford 6 as a yellowish solid (50%, 0.058 g, 0.15 mmol). Mp: 109–110 °C. $R_f = 0.59$ (10:1 hexane/*i*-PrOH). ¹H NMR (500 MHz, CDCl₃): δ 7.78-7.82 (m, 2H), 7.68-7.72 (m, 2H), 7.54–7.59 (m, 3H), 7.44–7.48 (m, 2H), 6.40 (d, $J_{\rm H-P}$ = 18.60 Hz, 1H). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 154.7 (d, J_{P-C} = 28.9 Hz, C), 135.59 (d, J_{P-C} = 87.9 Hz, C), 135.58 (d, J_{P-C} = 16.2 Hz, C), 132.8 (d, J_{P-C} = 3.1 Hz, CH), 132.7 (d, J_{P-C} = 1.8 Hz, CH), 133.2 (d, J_{P-C} = 11.7 Hz, CH), 130.8 (d, J_{P-C} = 12.7 Hz, CH), 129.1 (d, J_{P-C} = 12.9 Hz, CH), 128.9 (d, J_{P-C} = 9.2 Hz, CH), 127.4 (d, J_{P-C} = 84.4 Hz, C), 121.3 (d, $J_{P-C} = 10.4$ Hz, CH), 118.5 (q, $J_{P-C} = 321.4$ Hz, CF₃), 112.4 (d, $J_{P-C} = 78.8$ Hz, CH). ³¹P{¹H} NMR (202 MHz, CDCl₃): δ 41.0 (s). ¹⁹F NMR (470 MHz, CDCl₃): δ -72.92 (s). GC-MS (EI) m/z: 391 (7), 390 (34), 258 (22), 257 (100), 239 (14), 229 (31), 225 (21), 210 (17), 197 (27), 196 (47), 195 (15), 194 (37), 193 (17), 182 (26), 178 (49), 166 (25), 165 (82), 152 (39). HRMS (ESI/Q-TOF) m/z: calcd for C₁₅H₁₀O₃F₃PS₂ [M + H]⁺, 390.9834; found, 390.9834.

Reaction of 5 or 6 with Aryl Grignard Reagents (General Procedure E). To a Schlenk tube (25 mL) equipped with a magnetic stirrer and an argon inlet was added phosphine oxide **5** or **6** (0.13 mmol) in anhydrous THF (2 mL), and the mixture was cooled to 0 °C. Then, aryl Grignard reagent (0.195 mmol) was added. Then, the reaction mixture was stirred at 0 °C for 30–60 min. Then, the reaction mixture was quenched by the addition of NH₄Cl solution (5 mL) and extracted with CHCl₃ (5 × 5 mL). The collected organic phases were dried over Na₂SO₄, the solid was filtered off, and the was filtrate evaporated under reduced pressure. The crude reaction mixture was checked using the NMR technique. The residue was purified by column chromatography on silica gel using CHCl₃/ EtOAc/MeOH (30:5:1 v/v) or CHCl₃/MTBE (30:1 v/v) as an eluent.

(2-Ethynylphenyl)phenyl(p-tolyl)phosphine Oxide (8a). Compound 5a (0.0486 g, 0.13 mmol) was reacted with p-TolMgBr (0.195 mL, 0.195 mmol, 1 M solution in THF) according to general procedure E for 30 min to afford 8a (0.0403 g, 0.127 mmol, 98% yield) as a yellowish solid. Mp: 173-174 °C. $R_f = 0.45$ (30:5:1 CHCl₃/AcOEt/MeOH). ¹H NMR (500 MHz, CDCl₃): δ 7.71-7.75 (m, 2H), 7.59-7.68 (m, 4H), 7.40-7.56 (m, 5H), 7.26-7.28 (m, 2H), 3.00 (s, 1H), 2.41 (s, 3H). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 142.3 (d, J_{P-C} = 2.7 Hz, C), 134.9 (d, J_{P-C} = 100.8 Hz, C), 134.9 (d, $J_{P-C} = 9.1$ Hz, CH), 133.8 (d, $J_{P-C} = 9.1$ Hz, CH), 132.5 (d, $J_{P-C} =$ 106.3 Hz, C), 132.3 (d, J_{P-C} = 10.9 Hz, 2CH), 132.2 (d, J_{P-C} = 10.0 Hz, 2CH), 131.7 (d, J_{P-C} = 2.7 Hz, CH), 131.6 (d, J_{P-C} = 1.8 Hz, CH), 129.1 (d, J_{P-C} = 12.7 Hz, 2CH), 128.7 (d, J_{P-C} = 108.9 Hz, C), 128.4 (d, J_{P-C} = 11.8 Hz, CH), 128.3 (d, J_{P-C} = 11.8 Hz, CH), 125.3 (d, $J_{P-C} = 7.3$ Hz, C), 85.0 (s, C), 81.5 (d, $J_{P-C} = 5.5$ Hz, CH), 21.6 (s, CH₃). ³¹P{¹H} NMR (202 MHz, CDCl₃): δ 28.70 (s). GC–MS (EI) m/z: 317 (21), 316 (93) (M)⁺, 315 (100), 297 (15), 269 (13), 268 (15), 254 (18), 253 (18), 252 (15), 239 (34), 223 (17), 215 (11), 210 (12), 197 (11), 196 (19), 191 (11), 189 (11), 182 (15), 174 (17), 165 (32), 152 (21), 91 (24), 89 (12), 78 (15). HRMS (ESI/Q-TOF) m/z: calcd for C₂₁H₁₇OP [M + H]⁺, 317.1090; found, 317.1088.

(2-Ethynylphenyl)phenyl(m-tolyl)phosphine Oxide (8b). Compound 5a (0.0486 g, 0.13 mmol) was reacted with m-TolMgBr (0.195 mL, 0.195 mmol, 1 M solution in THF) according to general procedure E for 30 min to afford 8b (0.0345 g, 0.109 mmol, 84% yield) as a yellowish oil. $R_f = 0.65$ (2:1 CHCl₃/acetone). ¹H NMR (500 MHz, CDCl₃): δ 7.71–7.75 (m, 2H), 7.60–7.68 (m, 3H), 7.39-7.58 (m, 6H), 7.33-7.36 (m, 2H), 3.00 (s, 1H), 2.37 (s, 3H). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 138.2 (d, J_{P-C} = 11.8 Hz, C), 134.9 (d, J_{P-C} = 8.2 Hz, CH), 134.7 (d, J_{P-C} = 100.8 Hz, C), 133.8 (d, $J_{P-C} = 9.1$ Hz, CH), 132.6 (d, $J_{P-C} = 1.8$ Hz, CH), 132.59 (d, $J_{P-C} =$ 10.0 Hz, CH), 132.4 (d, J_{P-C} = 105.4 Hz, C), 132.15 (d, J_{P-C} = 10.0 Hz, 2CH), 134.7 (d, *J*_{P-C} = 100.8 Hz, C), 131.8 (d, *J*_{P-C} = 105.4 Hz, C), 131.7 (d, $J_{P-C} = 2.7$ Hz, CH), 131.6 (d, $J_{P-C} = 1.8$ Hz, CH), 129.3 (d, $J_{P-C} = 10.9$ Hz, CH), 128.4 (d, $J_{P-C} = 11.8$ Hz, CH), 128.3 (d, $J_{P-C} = 12.7$ Hz, 2CH), 128.1 (d, $J_{P-C} = 13.6$ Hz, CH), 125.3 (d, $J_{P-C} = 6.4$ Hz, C), 84.9 (s, C), 81.6 (d, $J_{P-C} = 6.4$ Hz, CH), 21.5 (s, CH₃). ³¹P{¹H} NMR (202 MHz, CDCl₃): δ 28.56 (s). GC–MS (EI) m/z: 317 (22), 316 (100) (M)⁺, 315 (97), 268 (20), 267 (13), 254 (11), 253 (24), 252 (17), 239 (28), 210 (15), 207 (11), 197 (14), 196 (35), 195 (11), 194 (10), 189 (12), 183 (14), 178 (26), 176 (19), 166 (11), 165 (48), 153 (12), 152 (42), 151 (16), 150 (12), 107 (16), 102 (12), 101 (12), 92 (35), 91 (67), 89 (40). HRMS (ESI/Q-TOF) m/z: calcd for $C_{21}H_{17}OP [M + Na]^+$, 339.0909; found, 339.0912.

(2-Ethynylphenyl)phenyl(o-tolyl)phosphine Oxide (8c). Compound 5a (0.0486 g, 0.13 mmol) was reacted with o-TolMgCl (0.195 mL, 0.195 mmol, 1 M solution in THF) according to general procedure E for 30 min to afford 8c (0.0156 g, 0.0494 mmol, 38% yield) as a yellowish oil. $R_f = 0.15$ (30:1 CHCl₃/MTBE). ¹H NMR (500 MHz, CDCl₃): δ 7.75-7.82 (m, 3H), 7.61-7.63 (m, 1H), 7.52-7.57 (m, 2H), 7.41-7.49 (m, 5H), 7.18-7.20 (m, 1H), 7.13-7.16 (m, 1H), 2.94 (s, 1H), 2.47 (s, 3H). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 143.2 (d, J_{P-C} = 8.2 Hz, C), 135.0 (d, J_{P-C} = 99.9 Hz, C), 134.9 (d, $J_{P-C} = 9.1$ Hz, CH), 133.7 (d, $J_{P-C} = 12.7$ Hz, CH), 133.4 (d, $J_{P-C} = 9.1$ Hz, CH), 132.4 (d, $J_{P-C} = 10.0$ Hz, CH), 131.9 (d, J_{P-C} = 2.7 Hz, CH), 131.8 (d, J_{P-C} = 2.7 Hz, CH), 131.55 (d, J_{P-C} = 10.9 Hz, CH), 131.51 (d, J_{P-C} = 7.3 Hz, CH), 130.4 (d, J_{P-C} = 105.4 Hz, C), 128.7 (d, $J_{P-C} = 11.8$ Hz, CH), 128.3 (d, $J_{P-C} = 12.7$ Hz, CH), 124.9 (d, $J_{P-C} = 12.7$ Hz, CH), 124.9 (d, $J_{P-C} = 7.3$ Hz, C), 84.7 (s, C), 81.4 (d, $J_{P-C} = 5.5$ Hz, CH), 21.7 (s, CH₃). ³¹P NMR (202 MHz, CDCl₃): δ 30.71 (s). GC-MS (EI) m/z: 317 (8), 316 (48) (M)⁺, 315 (100), 237 (17), 220 (11), 191 (16), 189 (14), 178 (11), 165 (21), 77 (11). HRMS (ESI/Q-TOF) m/z: calcd for C₂₁H₁₇OP [2M + Na]+, 655.1926; found, 655.1929.

[2-(Ethynyl)phenyl]diphenylphosphine Oxide (8d). Compound 5a (0.0486 g, 0.13 mmol) was reacted with PhMgBr (0.195 mL, 0.195 mmol, 1 M solution in THF) according to general procedure E for 30 min to afford 8d (0.0373 g, 0.124 mmol, 95% yield) as a yellowish solid. Mp: 181.9–182.9 °C. $R_f = 0.59 (2:1 \text{ CHCl}_3/\text{acetone})$. ¹H NMR (500 MHz, CDCl₃): δ 7.72-7.77 (m, 4H), 7.65-7.69 (m, 1H), 7.61-7.62 (m, 1H), 7.49-7.59 (m, 3H), 7.41-7.48 (m, 5H), 2.99 (s, 1H). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 134.9 (d, J_{P-C} = 9.1 Hz, CH), 134.7 (d, J_{P-C} = 100.8 Hz, C), 133.8 (d, J_{P-C} = 10.0 Hz, CH), 132.2 (d, $J_{P-C} = 10.0$ Hz, CH), 132.1 (d, $J_{P-C} = 106.2$ Hz, C), 131.8 (d, $J_{P-C} = 2.7$ Hz, CH), 131.6 (d, $J_{P-C} = 2.7$ Hz, CH), 128.5 (d, J_{P-C} = 11.8 Hz, CH), 128.3 (d, J_{P-C} = 12.7 Hz, CH), 125.3 (d, J_{P-C} = 6.4 Hz, C), 85.0 (s, C), 81.5 (d, J_{P-C} = 5.5 Hz, CH). ³¹P NMR (202 MHz, CDCl₃): δ 28.49 (s). GC-MS (EI) m/z: 303 (12), 302 (50) (M)⁺, 301 (46), 254 (12), 253 (12), 252 (12), 225 (17), 196 (24), 183 (16), 178 (17), 176 (14), 165 (31), 152 (27), 151 (15), 107 (13), 101 (11), 78 (44), 77 (93), 76 (15), 75 (33), 74 (17). HRMS (ESI/Q-TOF) m/z: calcd for C₂₀H₁₅OP [M + Na]⁺, 325.0753; found, 325.0754.

p-Anisyl(2-ethynylphenyl)phenylphosphine Oxide (8e). Compound **5a** (0.0486 g, 0.13 mmol) was reacted with *p-*AnMgBr (0.39 mL, 0.195 mmol, 0.5 M solution in THF) according to general procedure E for 30 min to afford **8e** (0.0419 g, 0.127 mmol, 98% yield) as a yellowish solid. Mp: 149.5–150.5 °C. $R_f = 0.58$ (2:1

CHCl₃/acetone). ¹H NMR (500 MHz, CDCl₃): δ 7.65-7.76 (m, 5H), 7.61-7.62 (m, 1H), 7.49-7.51 (m, 2H), 7.41-7.48 (m, 3H), 6.97-6.99 (m, 2H), 3.89 (s, 3H), 3.01 (s, 1H). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 162.5 (d, J_{P-C} = 2.7 Hz, C), 134.9 (d, J_{P-C} = 9.1 Hz, CH), 134.7 (d, J_{P-C} = 100.8 Hz, C), 134.2 (d, J_{P-C} = 10.9 Hz, 2CH), 133.8 (d, $J_{P-C} = 9.1$ Hz, CH), 132.3 (d, $J_{P-C} = 107.2$ Hz, C), 132.2 (d, $J_{P-C} = 100$ Hz, 2CH), 131.8 (d, $J_{P-C} = 2.7$ Hz, CH), 131.7 (d, $J_{P-C} = 2.7$ Hz, CH), 131.8 (d, $J_{P-C} = 2.7$ Hz, CH), 131.7 (d, $J_{P-C} = 2.7$ Hz, CH), 131.8 (d, $J_{P-C} = 2.7$ Hz, CH), 131.7 (d, $J_{P-C} = 2.7$ Hz, CH), 131.8 (d, $J_{P-C} = 2.7$ Hz, CH), 131.7 (d, $J_{P-C} = 2.7$ Hz, CH), 131.7 (d, $J_$ 2.7 Hz, CH), 128.5 (d, J_{P-C} = 10.9 Hz, CH), 128.3 (d, J_{P-C} = 11.8 Hz, 2CH), 125.2 (d, J_{P-C} = 7.3 Hz, C), 122.8 (d, J_{P-C} = 112.6 Hz, C), 113.9 (d, J_{P-C} = 13.6 Hz, 2CH), 85.0 (s, C), 81.6 (d, J_{P-C} = 5.5 Hz, CH), 55.3 (s, CH₃). ³¹P{¹H} NMR (202 MHz, CDCl₃): δ 28.15 (s). GC-MS (EI) m/z: 333 (22), 332 (100) (M)⁺, 331 (72), 317 (19), 284 (14), 270 (15), 255 (24), 253 (14), 252 (12), 241 (11), 240 (10), 239 (20), 231 (10), 226 (15), 196 (15), 194 (15), 184 (11), 183 (36), 178 (13), 176 (17), 170 (16), 169 (10), 165 (52), 163 (12), 157 (10), 152 (30), 151 (12), 141 (12), 139 (18), 125 (25), 120 (15), 15 (15), 108 (11), 107 (19), 101 (10), 95 (17), 92 (41), 78 (34), 77 (34), 76 (18). HRMS (ESI/Q-TOF) m/z: calcd for $C_{21}H_{17}O_2P [M + Na]^+$, 355.0856; found, 355.0856.

m-Anisyl(2-ethynylphenyl)phenylphosphine Oxide (8f). Compound 5a (0.0486 g, 0.13 mmol) was reacted with m-AnMgBr (0.195 mL, 0.195 mmol, 1 M solution in THF) according to general procedure E for 30 min to afford 8f (0.0385 g, 0.116 mmol, 89% yield) as a yellow solid. Mp: 129-130 °C. Rf = 0.69 (2:1 CHCl₃/ acetone). ¹H NMR (500 MHz, CDCl₃): δ 7.71-7.77 (m, 2H), 7.60-7.64 (m, 2H), 7.50-7.57 (m, 2H), 7.44-7.49 (m, 3H), 7.39-7.43 (m, 2H), 7.23-7.27 (m, 1H), 7.07-7.09 (m, 1H), 3.80 (s, 3H), 3.02 (s, 1H). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 159.4 (d, J_{P-C} = 14.5 Hz, C), 134.9 (d, J_{P-C} = 9.1 Hz, CH), 133.8 (d, J_{P-C} = 9.9 Hz, CH), 133.3 (d, J_{P-C} = 105.4 Hz, C), 132.1 (d, J_{P-C} = 9.9 Hz, 2CH), 132.0 (d, J_{P-C} = 103.5 Hz, C), 131.8 (d, J_{P-C} = 3.6 Hz, CH), 131.7 (d, J_{P-C} = 1.8 Hz, CH), 129.5 (d, J_{P-C} = 15.4 Hz, CH), 128.4 (d, J_{P-C} = 9.9 Hz, CH), 128.3 (d, J_{P-C} = 12.7 Hz, 2CH), 125.3 (d, J_{P-C} = 6.4 Hz, C), 124.5 (d, J_{P-C} = 10.0 Hz, CH), 118.1 (d, J_{P-C} = 2.7 Hz, CH), 116.9 (d, J_{P-C} = 10.9 Hz, CH), 85.1 (s, C), 81.5 (d, J_{P-C} = 6.4 Hz, CH), 55.4 (s, OCH₃). ³¹P{¹H} NMR (202 MHz, CDCl₃): δ 28.82 (s). GC-MS (EI) m/z: 334 (5), 333 (19), 332 (82) (M)⁺, 331 (83), 317 (21), 316 (11), 285 (11), 284 (16), 281 (17), 271 (10), 270 (20), 269 (13), 254 (16), 253 (24), 251 (16), 240 (12), 238 (29), 226 (18), 225 (18), 223 (16), 208 (11), 207 (40), 199 (10), 196 (21), 195 (13). HRMS (ESI/Q-TOF) m/z: calcd for $C_{21}H_{17}O_2P$ [M + Na]⁺, 355.0858; found, 355.0860.

o-Anisyl(2-ethynylphenyl)phenylphosphine Oxide (8g). Compound 5a (0.0486 g, 0.13 mmol) was reacted with o-AnMgBr (0.195 mL, 0.195 mmol, 1 M solution in THF) according to general procedure E for 30 min to afford 8g (0.0397 g, 0.119 mmol, 92% yield) as a yellow solid. Mp: 156.7–157.7 °C. R_f = 0.54 (2:1 CHCl₃/ acetone). ¹H NMR (500 MHz, CDCl₃): δ 7.84–7.88 (m, 2H), 7.70– 7.74 (m, 1H), 7.61-7.66 (m, 1H), 7.56-7.58 (m, 1H), 7.48-7.54 (m, 2H), 7.42-7.46 (m, 3H), 7.36-7.39 (m, 1H), 7.03-7.06 (m, 1H), 6.89–6.92 (m, 1H), 3.54 (s, 3H), 2.89 (s, 1H). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 161.1 (d, J_{P-C} = 3.6 Hz, C), 134.9 (d, J_{P-C} = 7.3 Hz, CH), 134.4 (d, J_{P-C} = 9.1 Hz, CH), 134.1 (d, J_{P-C} = 1.9 Hz, CH), 132.9 (d, J_{P-C} = 10.0 Hz, CH), 132.2 (d, J_{P-C} = 10.0 Hz, 2CH), 131.4 (d, J_{P-C} = 1.8 Hz, CH), 130.9 (d, J_{P-C} = 1.9 Hz, CH), 128.2 (d, $J_{P-C} = 11.8$ Hz, CH), 127.9 (d, $J_{P-C} = 12.7$ Hz, 2CH), 124.5 (d, J_{P-C} = 6.4 Hz, C), 120.8 (d, J_{P-C} = 11.8 Hz, CH), 111.7 (d, J_{P-C} = 6.4 Hz, CH), 84.0 (s, C), 81.4 (d, $J_{P-C} = 6.4$ Hz, CH), 55.3 (s, CH₃). ³¹P{¹H} NMR (202 MHz, CDCl₃): δ 26.19 (s). GC–MS (EI) m/z: 333 (10), 332 (42) (M)⁺, 331 (55), 254 (12), 253 (12), 252 (12), 225 (17), 196 (24), 183 (16), 178 (17), 176 (14), 165 (31), 152 (27), 151 (15), 107 (13), 101 (11), 78 (44), 77 (93), 76 (15), 75 (33), 74 (17). HRMS (ESI/Q-TOF) m/z: calcd for $C_{21}H_{17}O_2P$ [M + Na]⁺, 355.0858; found, 355.0851.

2-Ethynylphenyl(9-phenanthryl)phenylphosphine Oxide (**8**h). Compound **5a** (0.0486 g, 0.13 mmol) was reacted with 9-phenanthryl magnesium bromide (0.39 mL, 0.195 mmol, 0.5 M solution in THF) according to general procedure E for 30 min to afford **8h** (0.0366 g, 0.091 mmol, 70% yield) as a yellow solid. Mp: 192–193 °C (dec.). R_f = 0.25 (100:1 CHCl₃/MTBE). ¹H NMR (500 MHz, CDCl₃): δ 8.86–8.75 (m, 3H), 7.79–7.89 (m, 3H), 7.73–7.78 (m, 3H), 7.65– 7.68 (m, 1H), 7.62–7.64 (m, 1H), 7.57–7.60 (m, 2H), 7.42–7.55 (m, 5H), 2.84 (s, 1H). $^{13}C{}^{1H}$ NMR (125 MHz, CDCl₃): δ 137.0 (d, $J_{P-C} = 11.8$ Hz, CH), 135.0 (d, $J_{P-C} = 9.1$ Hz, CH), 134.8 (d, $J_{P-C} = 99.0$ Hz, C), 133.7 (d, $J_{P-C} = 10.0$ Hz, CH), 132.6 (d, $J_{P-C} = 10.0$ Hz, CH), 132.1 (d, $J_{P-C} = 2.7$ Hz, C), 132.0 (d, $J_{P-C} = 2.7$ Hz, CH), 131.9 (d, $J_{P-C} = 106.3$ Hz, C), 131.7 (d, $J_{P-C} = 1.8$ Hz, CH), 131.2 (d, $J_{P-C} = 9.1$ Hz, C), 130.5 (d, $J_{P-C} = 9.1$ Hz, C), 130.1 (s, CH), 129.7 (d, $J_{P-C} = 14.5$ Hz, C), 129.0 (s, CH), 128.6 (d, $J_{P-C} = 11.8$ Hz, CH), 128.5 (d, $J_{P-C} = 2.7$ Hz, CH), 128.4 (d, $J_{P-C} = 15.4$ Hz, CH), 126.9 (s, CH), 125.4 (d, $J_{P-C} = 6.4$ Hz, C), 123.0 (s, CH), 122.7 (s, CH), 84.7 (s, C), 81.5 (d, $J_{P-C} = 5.5$ Hz, CH). ${}^{31}P{}^{1}H{}$ NMR (202 MHz, CDCl₃): δ 31.94 (s). HRMS (ESI/Q-TOF) *m*/*z*: calcd for C₂₈H₁₉OP [2M + Na]⁺, 827.2239; found, 827.2228.

p-Chlorophenyl(2-ethynylphenyl)phenylphosphine Oxide (8i). Compound 5a (0.0486 g, 0.13 mmol) was reacted with p-Cl-C₆H₄MgBr (0.195 mL, 0.195 mmol, 1 M solution in THF) according to general procedure E for 30 min to afford 8i (0.0366 g, 0.107 mmol, 82% yield) as a yellow solid. Mp: 117.5-118 °C. $R_f = 0.55$ (2:1 CHCl₃/acetone). ¹H NMR (500 MHz, CDCl₃): δ 7.67-7.75 (m, 5H), 7.62-7.65 (m, 1H), 7.51-7.59 (m, 2H), 7.42-7.49 (m, 5H), 3.02 (s, 1H). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 138.4 (d, J_{P-C} = 3.6 Hz, C), 135.0 (d, J_{P-C} = 9.1 Hz, CH), 134.1 (d, J_{P-C} = 102.6 Hz, C), 133.8 (d, J_{P-C} = 9.1 Hz, CH), 133.6 (d, J_{P-C} = 10.9 Hz, CH), 132.15 (d, J_{P-C} = 10.0 Hz, CH), 132.12 (d, J_{P-C} = 3.1 Hz, CH), 131.9 (d, J_{P-C} = 2.5 Hz, CH), 131.0 (d, J_{P-C} = 106.3 Hz, C), 128.6 (d, J_{P-C} = 12.7 Hz, CH), 128.5 (d, J_{P-C} = 11.8 Hz, CH), 128.4 (d, J_{P-C} = 11.8 Hz, CH), 125.2 (d, J_{P-C} = 6.4 Hz, C), 85.3 (s, C), 81.5 (d, J_{P-C} = 6.4 Hz, CH). ${}^{31}P{}^{1}H{}^{1}NMR$ (202 MHz, CDCl₃): δ 27.61 (s). GC–MS (EI) m/z: 338 (17), 337 (32), 336 (61) (M)⁺, 335 (60), 250 (21), 253 (19), 252 (23), 225 (14), 212 (10), 199 (12), 196 (31), 194 (13), 183 (16), 178 (18), 176 (28), 169 (13), 165 (30), 152 (37), 150 (25), 119 (12). HRMS (ESI/Q-TOF) m/z: calcd for $C_{20}H_{14}ClOP [M + H]^+$, 337.0544; found, 337.0537.

2-Ethynylphenyl(p-fluorophenyl)phenylphosphine Oxide (8j). Compound 5a (0.0486 g, 0.13 mmol) was reacted with p-F-C₆H₄MgBr (0.195 mL, 0.195 mmol, 1 M solution in THF) according to general procedure E for 30 min to afford 8j (0.034 g, 0.107 mmol, 82% yield) as a yellow oil. $R_f = 0.52$ (30:5:1 CHCl₃/EtOAc/MeOH). ¹H NMR (500 MHz, $CDCl_3$): δ 7.68–7.77 (m, 5H), 7.61–7.64 (m, 1H), 7.51-7.58 (m, 2H), 7.42-7.49 (m, 3H), 7.13-7.17 (m, 2H), 3.01 (s, 1H). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 165.1 (dd, J_{P-C} = 3.6 Hz, $J_{\rm F-C}$ = 237.0 Hz, CF), 134.9 (d, $J_{\rm P-C}$ = 8.2 Hz, CH), 134.7 (dd, $J_{P-C} = 9.1$ Hz, $J_{F-C} = 11.8$ Hz, 2CH), 134.2 (d, $J_{P-C} = 100.8$ Hz, C), 133.7 (d, $J_{P-C} = 9.1$ Hz, CH), 132.1 (d, $J_{P-C} = 10.0$ Hz, 2CH), 132.0 (d, $J_{P-C} = 2.7$ Hz, CH), 131.9 (d, $J_{P-C} = 2.7$ Hz, CH), 131.8 (d, $J_{P-C} = 108.1$ Hz, C), 128.6 (d, $J_{P-C} = 11.8$ Hz, CH), 128.4 (d, $J_{P-C} = 11.8$ Hz, 128.4 (d, J_{P-C 11.8 Hz, 2CH), 128.1 (dd, J_{F-C} = 2.7 Hz, J_{P-C} = 108.9 Hz, C), 125.2 (d, $J_{P-C} = 6.4$ Hz, C), 115.7 (dd, J = 20.9 Hz, $J_{P-C} = 13.6$ Hz, CH), 85.2 (s, C), 81.5 (d, J_{P-C} = 5.5 Hz, CH). ³¹P{¹H} NMR (202 MHz, CDCl₃): δ 27.61 (s). GC-MS (EI) m/z: 321 (14), 320 (58) (M)⁺, 319 (68), 300 (16), 273 (15), 272 (20), 271 (19), 270 (15), 252 (11), 242 (18), 245 (18), 214 (23), 201 (20), 196 (28), 194 (20), 183 (20), 178 (11), 176 (17), 170 (19), 165 (26), 152 (26), 151 (13), 150 (16), 126 (11), 107 (17). HRMS (ESI/Q-TOF) m/z: calcd for $C_{20}H_{14}FOP [M + H]^+$, 321.0839; found, 321.0841.

(2-Ethynylphenyl)phenyl[p-(N,N-dimethylamino)phenyl]phosphine Oxide (**8**k). Compound **5a** (0.0486 g, 0.13 mmol) was reacted with p-Me₂N-C₆H₄MgBr (0.39 mL, 0.195 mmol, 0.5 M solution in THF) according to general procedure E for 30 min to afford **8k** (0.0269 g, 0.078 mmol, 60% yield) as a yellow solid. Mp: 194.9–195.7 °C. R_f = 0.42 (30:5:1 CHCl₃/EtOAc/MeOH). ¹H NMR (500 MHz, CDCl₃): δ 7.68–7.74 (m, 3H), 7.58–7.61 (m, 1H), 7.53–7.58 (m, 2H), 7.48–7.52 (m, 1H), 7.38–7.47 (m, 4H), 6.70– 6.72 (m, 2H), 3.02 (s, 6H), 3.02 (s, 1H). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 152.3 (d, J_{P-C} = 2.7 Hz, C), 135.8 (d, J_{P-C} = 100.8 Hz, C), 134.8 (d, J_{P-C} = 9.1 Hz, CH), 133.3 (d, J_{P-C} = 106.3 Hz, C), 132.1 (d, J_{P-C} = 10.0 Hz, 2CH), 131.3 (d, J_{P-C} = 2.7 Hz, CH), 131.2 (d, J_{P-C} = 1.8 Hz, CH), 128.3 (d, J_{P-C} = 11.8 Hz, CH), 128.1 (d, J_{P-C} = 11.8 Hz, 2CH), 125.2 (d, J_{P-C} = 6.4 Hz, C), 116.3 (d, J_{P-C} = 118.1 Hz, C), 111.1 (d, J_{P-C} = 12.7 Hz, 2CH), 84.6 (s, C), 81.8 (d, J_{P-C} = 5.5 Hz, CH), 39.9 (s, 2CH₃). ³¹P{¹H} NMR (202 MHz, CDCl₃): δ 28.92 (s). GC-MS (EI) *m*/*z*: 346 (18), 345 (100) (M)⁺, 344 (32), 330 (15), 329 (11), 252 (16), 183 (10), 152 (12), 136 (13), 77 (12), 51 (10). HRMS (ESI/Q-TOF) *m*/*z*: calcd for C₂₂H₂₀NOP [M + H]⁺, 346.1355; found, 346.1360.

(2-Ethynyl-6-methylphenyl)phenyl(p-tolyl)phosphine Oxide (10a). Compound 5b (0.0505 g, 0.13 mmol) was reacted with p-TolMgBr (0.195 mL, 0.195 mmol, 1 M solution in THF) according to general procedure E for 1 h to afford 10a (0.0283 g, 0.086 mmol, 66% yield) as a yellowish oil. $R_f = 0.15$ (200:1 CHCl₃/MTBE). ¹H NMR (500 MHz, CDCl₃): δ 7.68-7.72 (m, 2H), 7.59-7.63 (m, 2H), 7.50-7.54 (m, 1H), 7.39-7.43 (m, 3H), 7.33-7.36 (m, 1H), 7.24-7.27 (m, 3H), 2.61 (s, 1H), 2.59 (s, 3H), 2.41 (s, 3H). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 145.5 (d, J_{P-C} = 7.3 Hz, C), 142.3 (d, J_{P-C} = 3.6 Hz, C), 134.4 (d, J_{P-C} = 105.4 Hz, C), 133.6 (d, J_{P-C} = 9.1 Hz, CH), 133.1 (d, J_{P-C} = 10.0 Hz, CH), 132.1 (d, J_{P-C} = 10.0 Hz, 4CH), 131.6 (d, J_{P-C} = 2.7 Hz, CH), 131.1 (d, J_{P-C} = 2.7 Hz, CH), 130.5 (d, $J_{P-C} = 107.2 \text{ Hz}, \text{ C}), 129.1 \text{ (d, } J_{P-C} = 12.7 \text{ Hz}, 2\text{CH}), 129.1 \text{ (d, } J_{P-C} = 12.7 \text{ Hz}, 2\text{CH})$ 11.8 Hz, 2CH), 125.7 (d, J_{P-C} = 9.1 Hz, C), 84.6 (s, C), 82.1 (d, J_{P-C} = 6.4 Hz, CH), 23.3 (d, J_{P-C} = 4.5 Hz, CH), 21.6 (s, CH₃). ³¹P{¹H} NMR (202 MHz, CDCl₃): δ 30.67 (s). GC–MS (EI) m/z: 330 (1) (M)⁺, 329 (1), 305 (19), 304 (100), 303 (55), 302 (18), 289 (14), 288 (22), 273 (18), 258 (11), 257 (36), 256 (16), 242 (29), 241 (24), 240 (14), 239 (22), 227 (21), 213 (19), 197 (18), 196 (18), 194 (17), 183 (49), 178 (11), 170 (12), 166 (15), 165 (67), 164 (11), 163 (14), 152 (34), 139 (17), 91 (42), 89 (25), 78 (23), 77 (70). HRMS (ESI/Q-TOF) m/z: calcd for $C_{22}H_{19}OP$ [M + H]⁺, 331.1246; found, 331.1236.

(2-Ethynyl-6-methylphenyl]diphenylphosphine Oxide (10d). Compound 5b (0.0505 g, 0.13 mmol) was reacted with PhMgBr (0.195 mL, 0.195 mmol, 1 M solution in THF) according to general procedure E for 1 h to afford 10d (0.0374 g, 0.118 mmol, 91% yield) as a yellowish oil. $R_f = 0.15$ (200:1 CHCl₃/MTBE). ¹H NMR (500 MHz, CDCl₃): δ 7.70-7.74 (m, 4H), 7.52-7.55 (m, 2H), 7.40-7.46 (m, 5H), 7.33-7.38 (m, 1H), 7.27-7.30 (m, 1H), 2.61 (s, 1H), 2.60 (s, 3H). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 145.6 (d, $J_{P-C} = 7.3$ Hz, C), 134.4 (d, J_{P-C} = 1.8 Hz, C), 133.7 (d, J_{P-C} = 9.1 Hz, CH), 133.1 (d, $J_{P-C} = 9.1$ Hz, CH), 132.1 (d, $J_{P-C} = 10.9$ Hz, CH), 131.8 (d, $J_{P-C} = 2.7$ Hz, CH), 131.1 (d, $J_{P-C} = 1.8$ Hz, CH), 128.3 (d, J_{P-C} = 12.7 Hz, 2CH), 125.7 (d, J_{P-C} = 8.2 Hz, C), 84.6 (s, C), 82.0 (d, $J_{P-C} = 6.4$ Hz, CH), 23.3 (d, $J_{P-C} = 3.6$ Hz, CH₃). ³¹P{¹H} NMR (202 MHz, CDCl₃): δ 30.62 (s). GC-MS (EI) m/z: 317 (5) (M)⁺, 315 (4), 291 (11), 290 (95), 289 (53), 274 (17), 259 (11), 243 (28), 243 (13), 241 (13), 239 (13), 228 (24), 212 (34), 197 (11), 194 (17), 183 (45), 165 (51), 139 (18), 77 (100). HRMS (ESI/Q-TOF) m/z: calcd for C₂₁H₁₇OP [M + H]⁺, 317.1090; found, 317.1082.

(p-Anisyl)(2-ethynyl-6-methylphenyl]phenylphosphine Oxide (10e). Compound 5b (0.0505 g, 0.13 mmol) was reacted with p-AnMgBr (0.39 mL, 0.195 mmol, 0.5 M solution in THF) according to general procedure E for 1 h to afford 10e (0.0266 g, 0.0767 mmol, 59% yield) as a yellowish oil. $R_f = 0.15$ (200:1 CHCl₃/MTBE). ¹H NMR (500 MHz, CDCl₃): δ 7.62–7.72 (m, 4H), 7.50–7.53 (m, 1H), 7.40-7.44 (m, 3H), 7.33-7.38 (m, 1H), 7.25-7.27 (m, 1H), 6.94-6.96 (m, 2H), 3.85 (m, 3H), 2.66 (s, 1H), 2.59 (s, 3H). $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (125 MHz, CDCl₃): δ 162.5 (d, J_{P-C} = 3.6 Hz, C), 145.5 (d, $J_{P-C} = 7.3$ Hz, C), 134.7 (d, $J_{P-C} = 108.1$ Hz, C), 134.1 (d, $J_{P-C} =$ 10.9 Hz, 2CH), 133.7 (d, J_{P-C} = 9.1 Hz, CH), 133.0 (d, J_{P-C} = 10.0 Hz, CH), 132.5 (d, J_{P-C} = 99.9 Hz, C), 131.9 (d, J_{P-C} = 10.0 Hz, 2CH), 131.6 (d, J_{P-C} = 2.7 Hz, CH), 130.9 (d, J_{P-C} = 1.8 Hz, CH), 128.3 (d, J_{P-C} = 11.8 Hz, 2CH), 125.6 (d, J_{P-C} = 6.4 Hz, C), 113.2 (d, $J_{P-C} = 13.6$ Hz, 2CH), 84.4 (s, C), 82.2 (d, $J_{P-C} = 6.4$ Hz, CH), 56.3 (s, CH₃), 23.3 (d, $J_{P-C} = 3.6$ Hz, CH₃). ³¹P{¹H} NMR (202 MHz, CDCl₃): δ 30.21 (s). HRMS (ESI/Q-TOF) m/z: calcd for $C_{22}H_{19}O_2P [M + H]^+$, 347.1195; found, 347.1205.

(2-Éthynyl-6-methylphenyl)(4-chlorophenyl)phenylphosphine Oxide (10i). Compound **5b** (0.0505 g, 0.13 mmol) was reacted with p-Cl-C₆H₄MgBr (0.195 mL, 0.195 mmol, 1 M solution in THF) according to general procedure E for 1 h to afford **10**i (0.0296 g, 0.0845 mmol, 65% yield) as a yellowish oil. $R_f = 0.4$ (30:5:1 CHCl₃/AcOEt/MeOH). ¹H NMR (500 MHz, CDCl₃): δ 7.69–7.73 (m, 2H), 7.63–7.67 (m, 2H), 7.54–7.57 (m, 1H), 7.40–7.47 (m, 5H), 7.36–7.38 (m, 1H), 7.27–7.29 (m, 1H), 2.67 (m, 1H), 2.59 (s, 3H). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 145.6 (d, $J_{P-C} = 8.2$ Hz, C), 138.3 (d, $J_{P-C} = 3.6$ Hz, C), 133.7 (d, $J_{P-C} = 9.1$ Hz, CH), 133.6 (d, $J_{P-C} = 102.6$ Hz, C), 133.5 (d, $J_{P-C} = 10.9$ Hz, 2CH), 133.2 (d, $J_{P-C} = 10.0$ Hz, CH), 132.9 (d, $J_{P-C} = 106.3$ Hz, C), 131.9 (d, $J_{P-C} = 2.7$ Hz, CH), 131.8 (d, $J_{P-C} = 10.0$ Hz, 2CH), 131.3 (d, $J_{P-C} = 1.8$ Hz, CH), 128.6 (d, $J_{P-C} = 8.2$ Hz, C), 85.1 (s, C), 82.1 (d, $J_{P-C} = 6.4$ Hz, CH), 23.3 (d, $J_{P-C} = 3.6$ Hz, CH₃). ³¹P{¹H} NMR (202 MHz, CDCl₃): δ 29.69 (s). HRMS (ESI/Q-TOF) m/z: calcd for C₂₁H₁₆CIOP [M + H]⁺, 351.0700; found, 351.0694.

(2-Ethynyl-6-methylphenyl)[p-(N,N-dimethylamino)phenyl]phenylphosphine Oxide (10k). Compound 5b (0.0505 g, 0.13 mmol) was reacted with p-Me₂N-C₆H₄MgBr (0.39 mL, 0.195 mmol, 0.5 M solution in THF) according to general procedure E for 1 h to afford 10k (0.0327 g, 0.091 mmol, 70% yield) as a brownish waxy solid. Mp: 140.5–144.5 °C. $R_f = 0.21$ (10:1 CHCl₃/MTBE). ¹H NMR (500 MHz, CDCl₃): δ 7.66-7.70 (m, 2H), 7.51-7.55 (m, 2H), 7.47-7.50 (m, 1H), 7.38-7.41 (m, 3H), 7.30-7.33 (m, 1H), 7.23-7.30 (m, 1H), 6.69-6.71 (m, 2H), 3.01 (s, 6H), 2.67 (s, 1H), 2.60 (m, 3H). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 152.5 (d, $J_{P-C} = 2.7$ Hz, C), 145.3 (d, J_{P-C} = 7.3 Hz, C), 135.6 (d, J_{P-C} = 105.4 Hz, C), 133.6 (d, J_{P-C} = 9.1 Hz, CH), 133.5 (d, J_{P-C} = 11.8 Hz, 2CH), 133.2 (d, J_{P-C} = 99.0 Hz, C), 132.9 (d, J_{P-C} = 10.0 Hz, CH), 131.9 (d, J_{P-C} = 10.0 Hz, 2CH), 131.3 (d, J_{P-C} = 3.6 Hz, CH), 130.6 (d, J_{P-C} = 1.8 Hz, CH), 128.6 (d, J_{P-C} = 101.7 Hz, C), 128.1 (d, J_{P-C} = 12.7 Hz, 2CH), 123.1 (d, J_{P-C} = 8.2 Hz, C), 111.2 (d, J_{P-C} = 12.7 Hz, 2CH), 84.1 (s, C), 82.3 (d, J_{P-C} = 6.4 Hz, CH), 39.9 (s, 2CH₃), 23.3 (d, J_{P-C} = 4.5 Hz, CH₃). ${}^{31}P{}^{1}H{}$ NMR (202 MHz, CDCl₃): δ 31.06 (s). HRMS (ESI/Q-TOF) m/z: calcd for $C_{23}H_{22}NOP$ [M + H]⁺, 360.1512; found, 360.1515.

(2-Ethynyl-5-chlorophenyl)phenyl(p-tolyl)phosphine Oxide (11a). Compound 5c (0.053 g, 0.13 mmol) was reacted with p-TolMgBr (0.195 mL, 0.195 mmol, 1 M solution in THF) according to general procedure E for 1 h to afford 11a (0.0301 g, 0.086 mmol, 66% yield) as an orange solid. Mp: 160.4-161.8 °C. R_f = 0.45 (30:5:1 CHCl₃/AcOEt/MeOH). ¹H NMR (500 MHz, CDCl₃): δ 7.71-7.75 (m, 3H), 7.61-7.66 (m, 2H), 7.52-7.56 (m, 2H), 7.45-7.49 (m, 3H), 7.27–7.30 (m, 2H), 3.02 (m, 1H), 2.43 (m, 3H). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 142.8 (d, J_{P-C} = 2.7 Hz, C), 137.3 (d, J_{P-C} = 97.2 Hz, C), 136.1 (d, J_{P-C} = 10.0 Hz, CH), 136.1 (d, J_{P-C} = 14.5 Hz, C), 133.7 (d, $J_{P-C} = 10.0$ Hz, CH), 132.3 (d, $J_{P-C} = 10.0$ Hz, 2CH), 132.2 (d, $J_{P-C} = 10.0$ Hz, 2CH), 132.1 (d, $J_{P-C} = 2.7$ Hz, CH), 131.9 (d, $J_{P-C} = 108.9$ Hz, C), 131.8 (d, $J_{P-C} = 2.7$ Hz, CH), 129.3 (d, $J_{P-C} = 12.7$ Hz, 2CH), 128.4 (d, $J_{P-C} = 12.7$ Hz, 2CH), 128.1 (d, $J_{P-C} = 12.7$ Hz, 2CH), 128.4 (d, $J_{P-C} = 12.7$ Hz, 2CH), 128.1 (d, J_{P-C} 109.9 Hz, C), 123.5 (d, J_{P-C} = 6.4 Hz, C), 85.9 (s, C), 80.8 (d, J_{P-C} = 5.5 Hz, CH). ³¹P{¹H} NMR (202 MHz, CDCl₃): δ 27.47 (s). GC-MS (EI) *m*/*z*: 353 (8), 352 (31), 351 (52), 350 (95) (M)⁺, 349 (91), 331 (8), 302 (12), 273 (27), 268 (25), 258 (13), 256 (12), 252 (23), 244 (17), 230 (14), 215 (22), 212 (14), 210 (13), 199 (13), 196 (15), 194 (22), 189 (29), 176 (25), 165 (31). HRMS (ESI/Q-TOF) m/z: calcd for C₂₁H₁₆ClOP [M + H]⁺, 351.0700; found, 351.0693.

(2-Ethynyl-5-chlorophenyl]diphenylphosphine Oxide (11d). Compound **5c** (0.053 g, 0.13 mmol) was reacted with PhMgBr (0.195 mL, 0.195 mmol, 1 M solution in THF) according to general procedure E for 1 h to afford **11d** (0.032 g, 0.095 mmol, 73% yield) as an yellow oil. $R_f = 0.48$ (30:5:1 CHCl₃/AcOEt/MeOH). ¹H NMR (500 MHz, CDCl₃): δ 7.73–7.77 (m, 5H), 7.53–7.59 (m, 3H), 7.46–7.50 (m, 5H), 3.01 (s, 1H). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 136.9 (d, $J_{P-C} = 98.1$ Hz, C), 136.1 (d, $J_{P-C} = 10.0$ Hz, CH), 135.2 (d, $J_{P-C} = 14.5$ Hz, C), 133.7 (d, $J_{P-C} = 9.1$ Hz, CH), 132.2 (d, $J_{P-C} = 10.0$ Hz, 4CH), 132.17 (d, $J_{P-C} = 4.5$ Hz, 2CH), 131.9 (d, $J_{P-C} = 2.7$ Hz, CH), 131.4 (d, $J_{P-C} = 107.2$ Hz, 2C), 128.5 (d, $J_{P-C} = 12.7$ Hz, CH), ³¹P{¹H</sup> NMR (202 MHz, CDCl₃): δ 27.46 (s). GC–MS (EI) m/z: 338 (14), 337 (33), 336 (46) (M)⁺, 335 (41), 259 (13), 254 (15), 252 (12), 230 (11), 207 (17), 199 (13), 196 (14), 194 (12), 176 (12), 154 (17), 152 (14), 135 (14), 100 (11), 99 (37), 98 (10), 78 (59), 77 (100), 76 (15), 75 (22), 74 (23), 51 (89). HRMS (ESI/ Q-TOF) *m/z*: calcd for $C_{20}H_{14}ClOP [M + H]^+$, 337.0544; found, 337.0543.

(p-Anisyl)(2-ethynyl-5-chlorophenyl]phenylphosphine Oxide (11e). Compound 5c (0.053 g, 0.13 mmol) was reacted with p-AnMgBr (0.39 mL, 0.195 mmol, 0.5 M solution in THF) according to general procedure E for 1 h to afford 11e (0.0276 g, 0.0754 mmol, 58% yield) as an orange oil. $R_f = 0.54$ (30:5:1 CHCl₃/AcOEt/ MeOH). ¹H NMR (500 MHz, CDCl₃): δ 7.65-7.77 (m, 5H), 7.52-7.56 (m, 2H), 7.45-7.48 (m, 3H), 6.69-6.99 (m, 2H), 3.86 (s, 3H), 3.03 (s, 1H). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 162.7 (d, J_{P-C} = 3.6 Hz, C), 137.5 (d, J_{P-C} = 98.1 Hz, C), 136.2 (d, J_{P-C} = 10.0 Hz, CH), 135.2 (d, $J_{P-C} = 14.5$ Hz, C), 134.2 (d, $J_{P-C} = 11.8$ Hz, 2CH), 133.7 (d, J_{P-C} = 10.0 Hz, CH), 132.2 (d, J_{P-C} = 10.9 Hz, 2CH), 132.0 (d, J_{P-C} = 3.6 Hz, CH), 131.9 (d, J_{P-C} = 108.1 Hz, C), 131.8 (d, J_{P-C} = 2.7 Hz, CH), 128.4 (d, J_{P-C} = 12.7 Hz, 2CH), 123.4 (d, J_{P-C} = 6.4 Hz, C), 122.4 (d, J_{P-C} = 113.5 Hz, C), 114.1 (d, J_{P-C} = 13.6 Hz, 2CH), 85.6 (s, C), 80.8 (d, J_{P-C} = 4.5 Hz, CH), 55.4 (s, OCH₃). ³¹P{¹H} NMR (202 MHz, CDCl₃): δ 27.26 (s). GC–MS (EI) m/z: 368 (27), 367 (48), 366 (100) (M)⁺, 365 (76), 353 (13), 351 (23), 289 (24), 283 (11), 252 (10), 245 (12), 239 (15), 217 (12), 199 (25), 182 (11), 176 (19), 170 (10), 152 (11), 151 (10), 141 (14), 139 (11), 138 (10), 123 (37), 110 (11), 108 (24), 107 (13). HRMS (ESI/Q-TOF) m/z: calcd for C₂₁H₁₆ClO₂P [M + H]⁺, 367.0649; found, 367.0642.

(4-Chlorophenyl)(2-ethynyl-5-chlorophenyl]phenylphosphine Oxide (11i). Compound 5c (0.053 g, 0.13 mmol) was reacted with p-Cl-C₆H₄MgBr (0.195 mL, 0.195 mmol, 1 M solution in THF) according to general procedure E for 1 h to afford 11i (0.0289 g, 0.078 mmol, 60% yield) as an yellow oil. $R_f = 0.47 (30:5:1 \text{ CHCl}_3/$ AcOEt/MeOH). ¹H NMR (500 MHz, CDCl₃): δ 7.67-7.77 (m, 5H), 7.54–7.60 (m, 2H), 7.45–7.51 (m, 5H), 3.04 (s, 1H). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 138.7 (d, J_{P-C} = 3.6 Hz, C), 136.3 (d, $J_{P-C} = 10.0$ Hz, 2CH), 135.4 (d, $J_{P-C} = 15.4$ Hz, C), 133.7 (d, $J_{P-C} = 15$ 10.0 Hz, CH), 133.6 (d, J_{P-C} = 10.9 Hz, 2CH), 132.4 (d, J_{P-C} = 1.8 Hz, CH), 132.1 (d, J_{P-C} = 1.8 Hz, CH), 132.1 (d, J_{P-C} = 10.0 Hz, 2CH), 128.8 (d, J_{P-C} = 13.6 Hz, 2CH), 128.6 (d, J_{P-C} = 12.7 Hz, 2CH), 123.3 (d, J_{P-C} = 6.4 Hz, C), 86.2 (s, C), 80.7 (d, J_{P-C} = 5.5 Hz, CH). ${}^{31}P{}^{1}H$ NMR (202 MHz, CDCl₃): δ 26.56 (s). GC-MS (EI) m/z: 373 (13), 372 (18), 371 (59), 370 (100) (M)⁺, 369 (24), 355 (22), 354 (11), 334 (17), 325 (14), 297 (11), 288 (14), 283 (14), 266 (18), 264 (25), 252 (43), 243 (13), 241 (18), 235 (10), 230 (28), 216 (14), 207 (21), 199 (13), 197 (13), 196 (16), 177 (18), 174 (13), 175 (12), 174 (22), 166 (12), 159 (12), 152 (12), 137 (11), 136 (17), 133 (41), 126 (10), 119 (13), 113 (14), 112 (36), 111 (34), 108 (11), 107 (30), 99 (37), 98 (17), 78 (12), 77 (41), 76 (24), 75 (69), 74 (35), 72 (21). HRMS (ESI/Q-TOF) m/z: calcd for $C_{20}H_{13}Cl_2OP [M + H]^+$, 371.0154; found, 371.0145.

(2-Ethynyl-5-chlorophenyl)[p-(N,N-dimethylamino)phenyl]phenyl Phosphine Oxide (11k). Compound 5c (0.053 g, 0.13 mmol) was reacted with p-Me₂N-C₆H₄MgBr (0.39 mL, 0.195 mmol, 0.5 M solution in THF) according to general procedure E for 1 h to afford 11k (0.0296 g, 0.078 mmol, 60% yield) as an orange oil. $R_f = 0.21$ (10:1 CHCl₃/MTBE). ¹H NMR (500 MHz, CDCl₃): δ 7.77-7.78 (m, 1H), 7.70-7.74 (m, 2H), 7.50-7.58 (m, 4H), 7.43-7.46 (m, 3H), 6.72-6.74 (m, 2H), 3.03 (s, 7H). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 152.4 (d, J_{P-C} = 1.8 Hz, C), 138.1 (d, J_{P-C} = 92.6 Hz, C), 135.9 (d, J_{P-C} = 10.5 Hz, CH), 134.9 (d, J_{P-C} = 14.5 Hz, CH), 133.6 (d, $J_{P-C} = 10.0$ Hz, CH), 133.5 (d, $J_{P-C} = 10.9$ Hz, 2CH), 132.6 (d, $J_{P-C} = 107.2 \text{ Hz}, \text{ C}$, 132.1 (d, $J_{P-C} = 10.0 \text{ Hz}, 2\text{CH}$), 131.7 (d, $J_{P-C} =$ 2.7 Hz, CH), 131.4 (d, $J_{P-C} = 1.8$ Hz, CH), 128.2 (d, $J_{P-C} = 12.7$ Hz, 2CH), 123.1 (d, $J_{P-C} = 5.5$ Hz, C), 115.2 (d, $J_{P-C} = 118.0$ Hz, C), 111.1 (d, $J_{P-C} = 13.6$ Hz, 2C), 85.5 (s, C), 80.9 (d, $J_{P-C} = 5.5$ Hz, CH), 39.9 (s, 2CH₃).³¹P{¹H} NMR (202 MHz, CDCl₃): δ 27.79 (s). GC-MS (EI) m/z: 379 (22), 378 (4) (M)⁺, 377 (9), 362 (10), 292 (12), 281 (41), 253 (15), 208 (24), 207 (100), 193 (13), 191 (18), 135 (12), 133 (17), 95 (12), 73 (29). HRMS (ESI/Q-TOF) m/z: calcd for $C_{22}H_{19}CINOP [M + H]^+$, 380.0966; found, 380.0976.

(2-Ethynyl-4-methoxyphenyl]diphenylphosphine Oxide (12d). Compound 5d (0.0525 g, 0.13 mmol) was reacted with PhMgBr (0.195 mL, 0.195 mmol, 1 M solution in THF) according to general procedure E to afford 12d (0.035 g, 0.107 mmol, 82% yield) as a yellowish solid. Mp: 156.8–157.8 °C. R_f = 0.15 (10:1 CHCl₃/ MTBE). ¹H NMR (500 MHz, CDCl₃): δ 7.72–7.76 (m, 4H), 7.49– 7.56 (m, 3H), 7.44-7.48 (m, 4H), 7.13-7.14 (m, 1H), 6.92-6.94 (m, 1H), 3.86 (s, 3H), 2.99 (s, 1H). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 162.0 (d, $J_{P-C} = 2.7$ Hz, C), 135.8 (d, $J_{P-C} = 10.0$ Hz, CH), 132.4 (d, J_{P-C} = 107.2 Hz, 2C), 132.2 (d, J_{P-C} = 10.0 Hz, 4CH), 131.7 (d, J_{P-C} = 2.7 Hz, 2CH), 128.3 (d, J_{P-C} = 11.8 Hz, 4CH), 126.9 (d, J_{P-C} = 8.2 Hz, C), 125.7 (d, J_{P-C} = 107.2 Hz, C), 120.3 (d, $J_{P-C} = 10.0$ Hz, CH), 114.4 (d, $J_{P-C} = 12.7$ Hz, C), 84.7 (s, C), 81.7 (d, $J_{P-C} = 5.5$ Hz, CH), 55.5 (s, CH₃). ³¹P{¹H} NMR (202 MHz, $CDCl_3$): δ 28.27 (s). GC-MS (EI) m/z: 333 (22), 332 (100) (M)⁺, 331 (76), 316 (11), 285 (13), 281 (15), 270 (18), 255 (48), 253 (24), 239 (90), 208 (15), 207 (34), 183 (28), 165 (31), 163 (11), 152 (15), 77 (36). HRMS (ESI/Q-TOF) m/z: calcd for $C_{21}H_{17}O_2P [M + H]^+$, 333.1039; found, 333.1040.

(2-Ethynyl-4-methoxyphenyl)phenyl[p-(N,N-dimethylamino)phenyl]phosphine Oxide (12k). Compound 5d (0.0525 g, 0.13 mmol) was reacted with p-Me₂N-C₆H₄MgBr (0.39 mL, 0.195 mmol, 0.5 M solution in THF) according to general procedure E for 1 h to afford 12k (0.0311 g, 0.083 mmol, 64% yield) as an orange oil. $R_f =$ 0.57 (30:5:1 CHCl₃/AcOEt/MeOH). ¹H NMR (500 MHz, CDCl₃): δ 7.69–7.73 (m, 2H), 7.52–7.62 (m, 4H), 7.40–7.47 (m, 2H), 7.11– 7.12 (m, 1H), 6.90-6.92 (m, 1H), 6.69-6.71 (m, 2H), 3.82 (s, 3H), 3.01 (s, 6H), 2.99 (s, 1H). ${}^{13}C{}^{1}H{}$ NMR (125 MHz, CDCl₃): δ 161.7 (d, $J_{P-C} = 2.7$ Hz, C), 152.3 (d, $J_{P-C} = 2.7$ Hz, C), 135.8 (d, $J_{P-C} = 10.8$ Hz, CH), 133.9 (d, $J_{P-C} = 107.2$ Hz, C), 133.6 (d, $J_{P-C} =$ 10.9 Hz, 2CH), 132.2 (d, J_{P-C} = 10.0 Hz, 2CH), 131.2 (d, J_{P-C} = 2.7 Hz, CH), 128.1 (d, J_{P-C} = 11.8 Hz, CH), 127.3 (d, J_{P-C} = 106.3 Hz, C), 126.7 (d, J_{P-C} = 8.2 Hz, C), 120.1 (d, J_{P-C} = 10.0 Hz, CH), 117.0 (d, J_{P-C} = 118.1 Hz, C), 114.2 (d, J_{P-C} = 12.7 Hz, 2CH), 111.2 (d, $J_{P-C} = 13.6$ Hz, CH), 84.3 (s, C), 81.7 (d, $J_{P-C} = 5.5$ Hz, CH), 55.5 (s, CH₃), 39.9 (s, 2CH₃). ³¹P{¹H} NMR (202 MHz, CDCl₃): δ 28.45 (s). HRMS (ESI/Q-TOF) m/z: calcd for C₂₃H₂₂NO₂P [M + H]⁺, 376.1461; found, 376.1460.

Reaction of 5a with *p***-TolMgBr at** -78 °C (General **Procedure F).** To a Schlenk tube (25 mL) equipped with a magnetic stirrer and an argon inlet was added phosphine oxide **5a** (0.0485 g, 0.13 mmol) in anhydrous THF (2 mL), and the mixture was cooled to -78 °C. Then, *p*-TolMgBr (0.195 mL, 0.195 mmol, 1 M solution in THF) was added. Then, the reaction mixture was stirred at -78 °C for 30 min. Then, the reaction mixture was quenched by the addition of NH₄Cl solution (5 mL) and extracted with CHCl₃ (5 × 10 mL). The collected organic phases were dried over Na₂SO₄, the solid was filtered off, and the filtrate was evaporated under reduced pressure. The crude reaction mixture was checked using the ³¹P NMR technique. The residue was purified by column chromatography on silica gel using CHCl₃/EtOAc/MeOH (30:5:1 v/ v) to provide **8a** (0.0148 g, 0.047 mmol, 36% yield) and **9**.

(2-Ethynylphenyl)(phenyl)((2-(phenyl(p-tolyl)phosphoryl)phenyl)ethynyl)phosphine Oxide (9): 0.0204 g, 0.038 mmol, 29% yield, white solid (EtOAc). Mp: $233-234 \degree C$ (dec). $R_f = 0.27$ (30:5:1 CHCl₃/AcOEt/MeOH). ¹H NMR (500 MHz, CDCl₃): δ 8.09–8.17 (m, 1H), 7.78-7.82 (m, 1H), 7.60-7.68 (m, 4H), 7.45-7.75 (m, 10H), 7.33–7.43 (m, 4H), 7.15–7.20 (m, 2H), 3.20 (d, J_{P-H}= 1.89 Hz, 1H), 2.35 (d, J_{P-H} = 5.04 Hz, 3H). ¹³C{¹H} NMR (125 MHz, $CDCl_3$): δ 142.7 (d, J_{P-C} = 2.7 Hz, C), 136.2 (d, J_{P-C} = 8.2 Hz, CH), 135.4 (d, J_{P-C} = 99.9 Hz, C), 134.4 (dd, J_{P-C} = 1.8 Hz, J_{P-C} = 11.8 Hz, CH), 133.9 (d, J_{P-C} = 10.0 Hz, CH), 133.4 (d, J_{P-C} = 10.0 Hz, CH), 132.2 (d, J_{P-C} = 3.6 Hz, CH), 132.1 (d, J_{P-C} = 10.0 Hz, 2CH), 132.07 (d, J_{P-C} = 2.7 Hz, CH), 132.06 (d, J_{P-C} = 3.08 Hz, CH), 131.9 (d, $J_{P-C} = 2.7$ Hz, CH), 131.85 (dd, $J_{P-C} = 4.5$ Hz, $J_{P-C} = 124.4$ Hz, C), 131.8 (d, $J_{P-C} = 2.7$ Hz, CH), 131.7 (d, $J_{P-C} = 1.8$ Hz, CH), 131.6 (d, J_{P-C} = 11.8 Hz, 2CH), 129.9 (d, J_{P-C} = 1.8 Hz, J_{P-C} = 11.8 Hz, CH), 129.32 (d, J_{P-C} = 13.6 Hz, 2CH), 128.5 (d, J_{P-C} = 12.7 Hz, 2CH), 128.1 (d, J_{P-C} = 2.7 Hz, CH), 128.1 (d, J_{P-C} = 2.7 Hz, CH), 127.4 (d, J_{P-C} = 8.2 Hz, C), 123.9 (dm, C), 102.5 (dd, J_{P-C} = 4.5 Hz, $J_{P-C} = 29.1 \text{ Hz}, \text{ C}$), 89.3 (d, $J_{P-C} = 172.6 \text{ Hz}, \text{ C}$), 85.6 (s, C), 80.7 (dd, $J_{P-C} = 2.7 \text{ Hz}, J_{P-C} = 7.3 \text{ Hz}, \text{ CH}$), 21.6 (s, CH₃). ³¹P{¹H} NMR (202 MHz, CDCl₃): δ 29.41 (d, $J_{P-P} = 12.4 \text{ Hz}$), 7.44 (d, $J_{P-P} = 12.4 \text{ Hz}$). HRMS (ESI/Q-TOF) m/z: calcd for $C_{35}H_{26}O_2P_2$ [M + H]⁺, 541.1481; found, 541.1479.

Reaction of 5a with *p*-TolMgBr in a Higher Scale (General Procedure G). To a Schlenk tube (25 mL) equipped with a magnetic stirrer and an argon inlet phosphine was added oxide 5a (0.24 g, 0.634 mmol) in anhydrous THF (5 mL), and the mixture was cooled to 0 °C. Then, *p*-TolMgBr (0.952 mL, 0.952 mmol, 1 M in THF) was added dropwise. Then, the reaction mixture was stirred at 0 °C for 1 h. Then, the reaction mixture was quenched by the addition of NH₄Cl solution (5 mL) and extracted with CHCl₃ (5 × 5 mL). The collected organic phases were dried over Na₂SO₄, the solid was filtered off, and the filtrate was evaporated under reduced pressure. The crude reaction mixture was checked using the ³¹P{¹H} NMR technique. The residue was purified by column chromatography on silica gel using CHCl₃/EtOAc/MeOH (30:5:1 v/v) as an eluent, yielding (2-ethynylphenyl)phenyl(*p*-tolyl)phosphine oxide (8a) in 91% yield (0.182 g, 0.577 mmol).

Reaction of 5a with PhLi or EtMgBr (General Procedure H). To a Schlenk tube (25 mL) equipped with a magnetic stirrer and an argon inlet was added phosphine oxide **5a** (0.0405 g, 0.108 mmol) in anhydrous THF (2 mL), and the mixture was cooled to 0 °C. Then, PhLi or EtMgBr (0.164 mmol) was added. Then, the reaction mixture was stirred at 0 °C for 30 min. Then, the reaction mixture was quenched by the addition of NH₄Cl solution (5 mL) and extracted with CHCl₃ (5 × 10 mL). The collected organic phases were dried over Na₂SO₄, the solid was filtered off, and the filtrate was evaporated under reduced pressure. The crude reaction mixture was checked using the ³¹P{¹H} NMR technique. The residue was purified by column chromatography on silica gel using CHCl₃/MTBE (30:1 v/v).

[2-(Ethynyl)phenyl]diphenylphosphine Oxide (8d). Compound Sa (0.0405 g, 0.108 mmol) was reacted with PhLi(0.086 mL, 0.164 mmol, 1.9 M solution in *n*-Bu₂O) according to general procedure H to afford 8d (0.007 g, 0.022 mmol, 21% yield).

Ethyl(2-ethynylphenyl)phenylphosphine (13). Compound 5a (0.0405 g, 0.108 mmol) was reacted with EtMgBr (0.162 mL, 0.162 mmol, 1 M solution in THF) according to general procedure H to afford 13 (0.016 g, 0.063 mmol, 58% yield) as a yellow oil. $R_f =$ 0.35 (30:5:1 CHCl₃/AcOEt/MeOH). ¹H NMR (500 MHz, CDCl₃): δ 8.18-8.24 (m, 1H), 7.71-7.76 (m, 2H), 7.56-7.91 (m, 1H), 7.46-7.55 (m, 3H), 7.40-7.44 (m, 2H), 3.21 (s, 1H), 2.71-2.80 (m, 1H), 2.51–2.61 (m, 1H), 1.20 (dt, $J_{H-H} = 7.72$ Hz, $J_{H-P} = 17.9$ Hz, 3H). ³¹P{¹H} NMR (202 MHz, CDCl₃): δ 34.50 (s). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 134.7 (d, J_{C-P} = 8.62 Hz, CH), 133.9 (d, J_{C-P} = 92.6 Hz, C), 133.8 (d, J_{C-P} = 6.8 Hz, CH), 133.1 (d J_{C-P} = 99.9 Hz, C), 131.6 (d, J_{C-P} = 2.5 Hz, CH), 131.5 (d, J_{C-P} = 2.5 Hz, CH), 130.9 (d, J_{C-P} = 9.99 Hz, 2CH), 128.9 (d, J_{C-P} = 10.0 Hz, CH), 128.3 (d, J_{C-P} = 12.7 Hz, 2CH), 123.2 (d, J_{C-P} = 8.2 Hz, C), 84.2 (s, C), 82.3 (d, J_{C-P} = 4.5 Hz, CH), 21.0 (d, J_{C-P} = 72.7 Hz, CH₂), 5.59 (d, J_{C-P} = 5.5 Hz, CH₃). GC-MS (EI) m/z: (%) 255 (9), 254 (49) (M)⁺, 253 (9), 226 (35), 225 (100), 179 (17), 178 (30), 165 (17), 152 (12), 149 (11), 77 (25). HRMS (ESI/Q-TOF) m/z: calcd for $C_{32}H_{30}O_2P_2Na$ $[2M + Na]^+$, 531.1619; found, 531.1628.

ASSOCIATED CONTENT

1 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.1c01629.

¹H NMR, ¹³C{¹H} NMR, ³¹P{¹H} NMR, and ¹⁹F NMR spectra for all products, crystallographic data (PDF)

Accession Codes

CCDC 2094907 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cam-

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Notes

The authors declare no competing financial interest.

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