

Palladium-Catalyzed Decarbonylative Sonogashira Alkynylation of Carboxylic–Phosphoric Anhydrides

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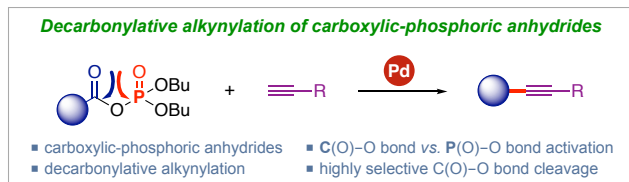
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We report the first palladium-catalyzed decarbonylative alkynylation of carboxylic–phosphoric anhydrides via highly selective C(O)–O bond cleavage. Carboxylic–phosphoric anhydrides are highly active carboxylic acid derivatives, which are generated through activating carboxylic acids using phosphates by esterification or direct dehydrogenative coupling with phosphites. Highly valuable internal alkynes have been generated by the present method, and the efficiency of this approach has been demonstrated through wide substrate scope and excellent functional group tolerance.

Introduction

Alkynes are one of the most fundamental functional groups through the field of organic synthesis, where their privileged status is gained through the presence of the versatile carbon–carbon triple bond.¹ Due to their unique properties, alkynes can undergo a plethora of mono- and difunctionalization reactions of broad utility in drug discovery, biochemistry and materials science, such as coupling, addition, cyclization, polymerization.² Principally, alkynes can be classified into terminal and internal alkynes. Terminal alkynes are commercially available, while most internal alkynes are not available. Therefore, the development of methods for the synthesis of internal alkynes has been particularly desirable over the past decades.³ In particular, Sonogashira cross-coupling represents the most widely employed, direct and efficient alkynylation method, underscoring the importance of this method throughout the realm of organic synthesis.⁴

Traditionally, aryl halides and pseudohalides have been used as classic electrophiles for the synthesis of internal alkynes via Sonogashira cross-coupling.^{5,6} However, due to their limitations, recently, orthogonal, more stable and more sustainable carboxylic acids and their derivatives have been employed as a new powerful class of cross-coupling reagents.^{7,8} In this activation manifold, cross-coupling reactions of carboxylic acids can be broadly categorized into decarboxylative couplings ($-\text{CO}_2$) and decarbonylative couplings ($-\text{CO}$).⁹ Owing to lower substrate generality and higher activation energy requirements of decarboxylative couplings, decarbonylative cross-coupling of carboxylic acids represents the most desirable choice of activating carboxylic acids as electrophilic reagents for cross-coupling reactions.¹⁰⁻¹³

In 2018, Chen group developed palladium-catalyzed decarbonylative alkynylation of amides using a series of amides, including *N*-acyl glutarimides, *N*-acyl succinimides, and *N*-acyl saccharins well tolerated by this method (Figure 1A).¹⁴ In 2021, a palladium-catalyzed decarbonylative alkynylation of carboxylic acids via $\text{C}(\text{O})-\text{O}$ bond cleavage was reported with the key to this reaction involving activation of carboxylic acids by acetic anhydride (Figure 1B).¹⁵ Simultaneously, we reported palladium-catalyzed decarbonylative alkynylation of carboxylic acids using pivalic anhydride to effect

activation of the C(O)–O bond (Figure 1C).¹⁶ In 2023, our group developed a robust palladium-catalyzed decarbonylative alkynylation of aryl anhydrides, which exhibits higher activity than carboxylic acids, amides, and esters (Figure 1D).¹⁷

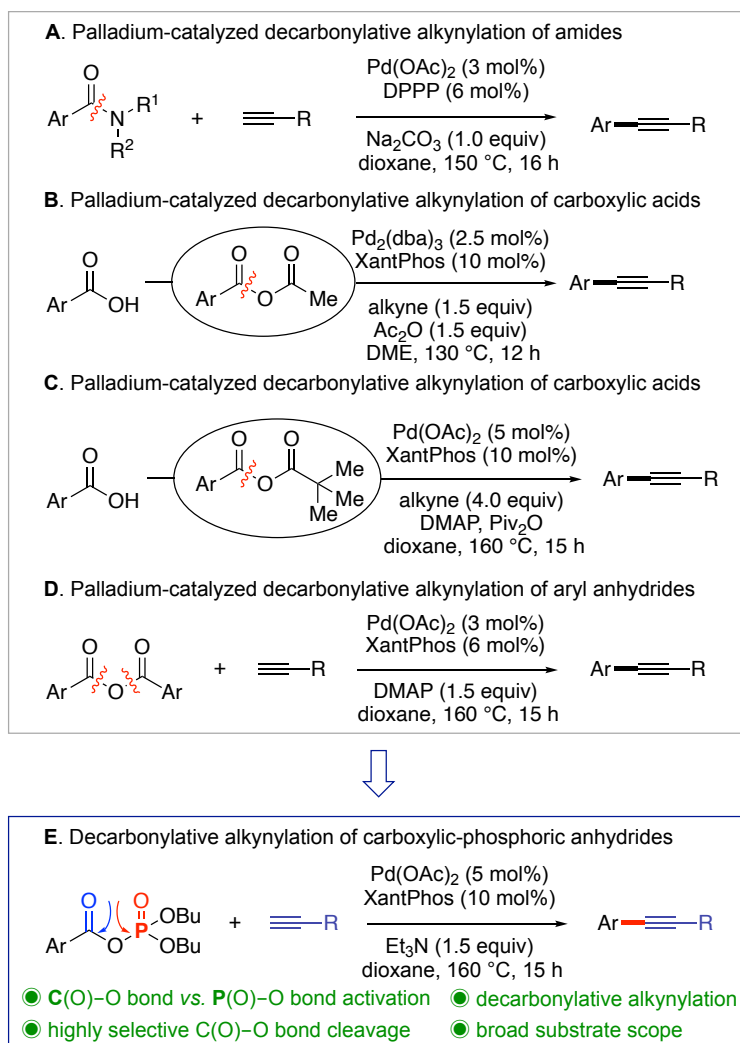


Figure 1. Metal-catalyzed decarbonylative alkynylation.

Based on our interest in this field, we found that acid anhydrides show the highest reactivity in decarbonylative alkynylation reactions.^{16,17} Therefore, we questioned whether carboxylic–phosphoric anhydrides can be utilized as a novel class of efficient substrates in decarbonylative alkynylation reactions (Figure 1E). The key difference between acid anhydrides and carboxylic–phosphoric anhydrides stems from the substitution of the central oxygen atom, which is flanked by two carbonyl groups in symmetrical anhydrides, while it is connected to a C=O carbonyl group and a P=O phosphoryl group in carboxylic–phosphoric anhydrides.^{18–19} For acid anhydrides, the insertion of a transition metal

into the two C(O)–O bonds is not selective, however, we hypothesized that for carboxylic–phosphoric anhydrides, the C(O)–O bond could selectively favor the insertion of a metal over the P(O)–O bond. This may be due to the stronger electron-withdrawing ability of C=O bonds compared to P=O bonds, resulting in stronger electrophilicity, thus C(O)–O bonds are easier to be cleaved compared to P(O)–O bonds.

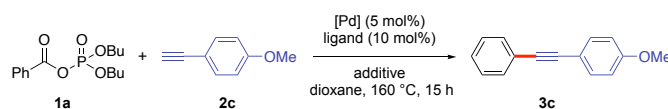
Herein, we report the first palladium-catalyzed decarbonylative alkynylation of carboxylic–phosphoric anhydrides via highly selective C(O)–O bond cleavage. Noteworthy features of this robust method include 1) the first decarbonylative process of carboxylic–phosphoric anhydrides to generate highly desirable internal alkynes, 2) highly selective C(O)–O vs. P(O)–O bond cleavage, and 3) one of the most reactive carboxylic acid derivatives for decarbonylative alkynylation.

Results and Discussion

The decarbonylative alkynylation of carboxylic–phosphoric anhydrides was first investigated using benzoic-(dibutyl phosphoric) anhydride (**1a**) and 1-ethynyl-4-methoxybenzene (**2c**) as model substrates (Table 1). The effect of base was first optimized, and triethyl amine (Et₃N) was to be the optimal base for this transformation (entries 1-7). Subsequently, we screened various phosphine ligands (entries 2, 8-20), and found XantPhos to be the optimal ligand for this transformation. It is noteworthy that dioxane was more effective as compared to toluene as a solvent (entries 2, 21). Furthermore, catalyst:ligand ratio of 1:2 was found as the best ratio under these conditions (entries 2, 22-23). Interestingly, increasing the amount of base resulted in a decrease in the yield of the reaction (entry 24). The optimal conditions involve carboxylic–phosphoric anhydride **1** (1.0 equiv), terminal alkyne **2** (3.0 equiv), Pd(OAc)₂ (5 mol%), XantPhos (10 mol%), triethyl amine (1.5 equiv), dioxane, 160 °C, 15 h. It is further noteworthy that carboxylic–phosphoric anhydrides are generated in an orthogonal way to other activated carboxylic acid derivatives by esterification with phosphates or direct dehydrogenative coupling with phosphites, and that the products resulting from the unselective P(O)–O bond cleavage were not detected under these reaction conditions. Interestingly, XanthPhos is the preferred ligand. In our experience, XanthPhos

is often the preferred biphosphine for decarbonylative coupling. This likely arises from the combined electronic and steric effect of the XantPhos family of ligands on decarbonylation of acyl-metals.

Table 1. Optimization of decarbonylative alkynylation^a



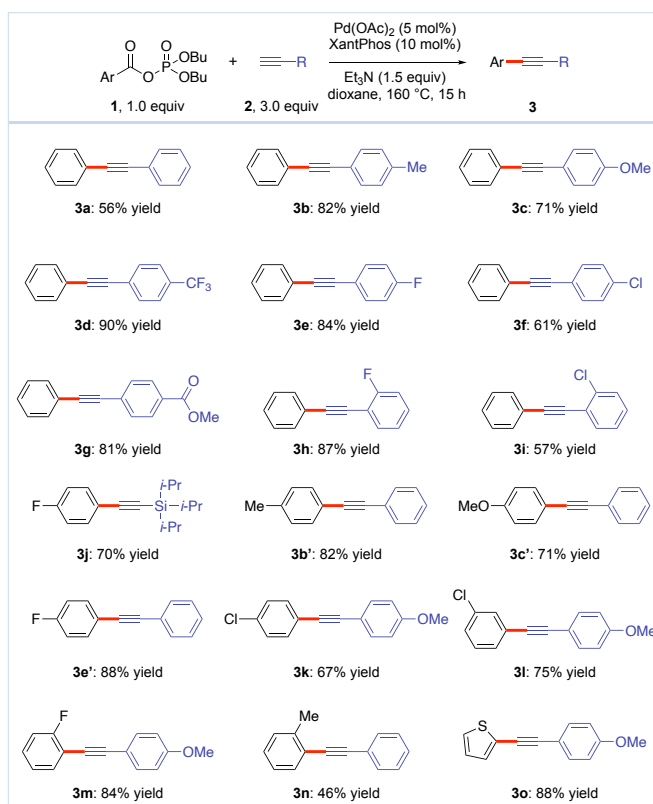
entry	catalyst	ligand	base	yield(%)
1	Pd(OAc) ₂	XantPhos		46
2	Pd(OAc) ₂	XantPhos	Et ₃ N	71
3	Pd(OAc) ₂	XantPhos	DMAP	21
4	Pd(OAc) ₂	XantPhos	Pyridine	24
5	Pd(OAc) ₂	XantPhos	Na ₂ CO ₃	27
6	Pd(OAc) ₂	XantPhos	K ₂ CO ₃	<5
7	Pd(OAc) ₂	XantPhos	K ₃ PO ₄	<5
8	Pd(OAc) ₂	DPPP	Et ₃ N	16
9	Pd(OAc) ₂	DPPB	Et ₃ N	30
10	Pd(OAc) ₂	DPPent	Et ₃ N	36
11	Pd(OAc) ₂	DPPF	Et ₃ N	40
12	Pd(OAc) ₂	BINAP	Et ₃ N	30
13	Pd(OAc) ₂	DavePhos	Et ₃ N	15
14	Pd(OAc) ₂	XPhos	Et ₃ N	17
15	Pd(OAc) ₂	SPhos	Et ₃ N	31
16	Pd(OAc) ₂	PCy ₃ HBF ₄	Et ₃ N	30
17	Pd(OAc) ₂	PCyPh ₂	Et ₃ N	55
18	Pd(OAc) ₂	PPh ₃	Et ₃ N	30
19	Pd(OAc) ₂	P(<i>t</i> -Bu) ₃ HBF ₄	Et ₃ N	32
20	Pd(OAc) ₂	P(2-furyl) ₃	Et ₃ N	45
21 ^b	Pd(OAc) ₂	XantPhos	Et ₃ N	22
22 ^c	Pd(OAc) ₂	XantPhos	Et ₃ N	56
23 ^d	Pd(OAc) ₂	XantPhos	Et ₃ N	36
24 ^e	Pd(OAc) ₂	XantPhos	Et ₃ N	48

^aStandard conditions: **1a** (1.0 equiv), **2a** (3.0 equiv), Pd(OAc)₂ (5 mol%), ligand (10 mol%), base (1.5 equiv), dioxane, 160 °C, 15 h; ^btoluene; ^cligand (5 mol%); ^dligand (15 mol%); ^ebase (4.0 equiv).

With the optimal conditions in hand, the substrate scope of this novel palladium-catalyzed decarbonylative alkynylation of carboxylic-phosphoric anhydrides was next investigated (Scheme 1). As shown, desired products bearing electron-neutral (**3a–b**), electron-donating (**3c**), and electron-withdrawing (**3d**) substituents could be well tolerated in this method. Furthermore, internal alkynes containing sensitive fluoro (**3e**, **3h**), chloro (**3f**, **3i**), and ester (**3g**) groups could be readily employed in this approach. In addition, sterically-hindered (**3h–i**) internal alkynes were also found compatible with this process. Pleasingly, the method is not limited to aromatic alkynes and silylacetylenes, such as

ethynyltriisopropylsilane (**3j**), could also be readily employed, delivering the valuable silylated internal alkynes. After screening the substrate scope of terminal alkynes, the substrate scope of carboxylic-phosphoric anhydrides was next tested. As shown, carboxylic-phosphoric anhydrides bearing electron-neutral (**3b'**), electron-rich (**3c'**), and electron-deficient (**3e'**) substituents could be readily employed in this transformation. Moreover, carboxylic-phosphoric anhydrides containing sensitive fluoro (**3e'**, **3m**), and chloro (**3k-l**) groups could be well tolerated by this method. Notably, sterically-hindered (**3n**) and heterocyclic (**3o**) substrates are also compatible with this approach. It should be noted that alkyl carboxylic-phosphoric anhydrides are not tolerated due to β -hydride elimination. At the present stage, alkyl alkynes are not compatible.

Scheme 1. Scope of Decarbonylative Alkynylation^a

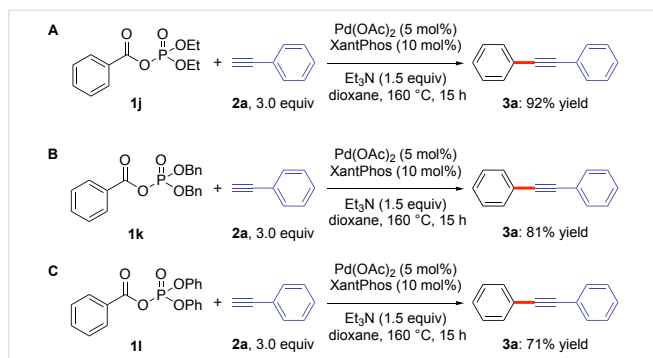


^aCondition: carboxylic-phosphoric anhydrides (0.2 mmol, 1.0 equiv), alkynes (3.0 equiv), Pd(OAc)₂ (5 mol%), XantPhos (10 mol%), dioxane (0.2 M), 160 °C, 15 h.

After identifying the substrate scope of terminal alkynes and carboxylic-phosphoric anhydrides, we also tested the effect of the phosphoryl group of carboxylic-phosphoric anhydrides for the reaction (Scheme 2). Importantly, when the substituent of the phosphonate group of carboxylic phosphoric-

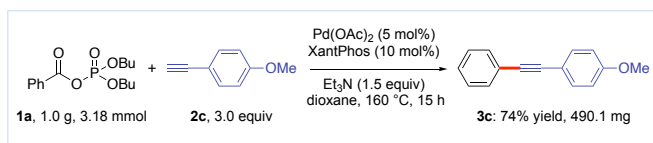
anhydride is less hindered diethyl group, 91% yield could be achieved under the standard conditions (Scheme 2A). Notably, the yield of the reaction could be 81% and 71%, respectively, when benzyl or phenyl phosphonates are used as the substituents of the phosphoryl group (Scheme 2B-C).

Scheme 2. Scope of P(O)–O Carboxylic–Phosphoric Anhydrides



To demonstrate the practicality of the method, the amount of reaction was increased to 1 gram, and the experimental results showed that excellent conversion can still be achieved at gram scale (Scheme 3).

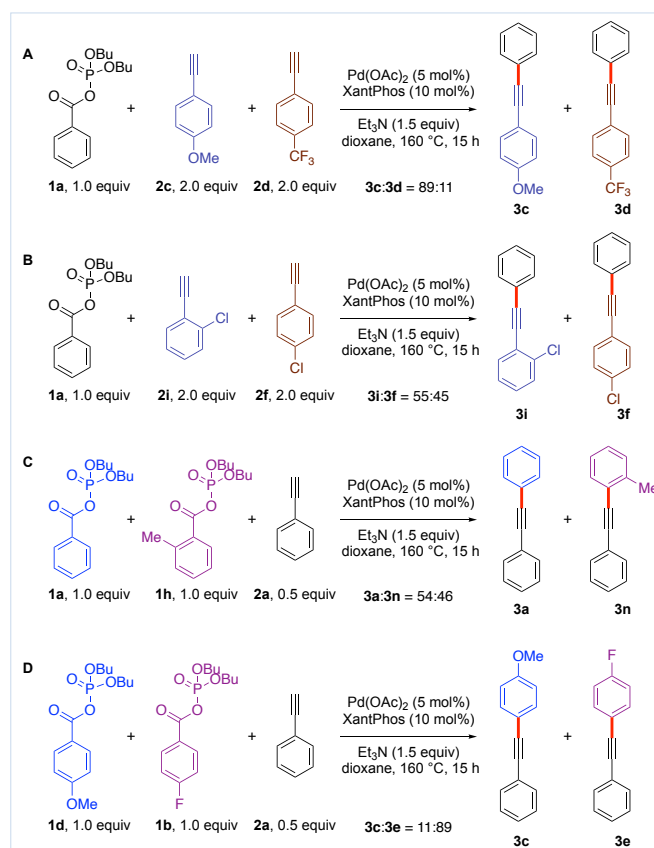
Scheme 3. Gram Scale Experiment



In order to gain insight into this transformation, competition experiments were conducted (Scheme 4). The electronic effect on terminal alkynes was first investigated, and the results showed that electron-rich alkynes are favored in this reaction (Scheme 4A). This is because alkynes with electron-donating substituents have stronger nucleophilicity, making it easier for them to coordinate with the metal center and squeeze out weaker nucleophilic groups during the transmetalation step. Next, the steric hindrance of the terminal alkyne was investigated, and the results showed that the steric hindrance of the terminal alkyne did not have a significant impact on the reaction, and *ortho*-substituted substrates showed slightly higher reactivity (Scheme 4B). Likewise, steric hindrance on the carboxylic–phosphoric anhydride had a little effect on the reaction, and *ortho*-unsubstituted substrates were more reactive

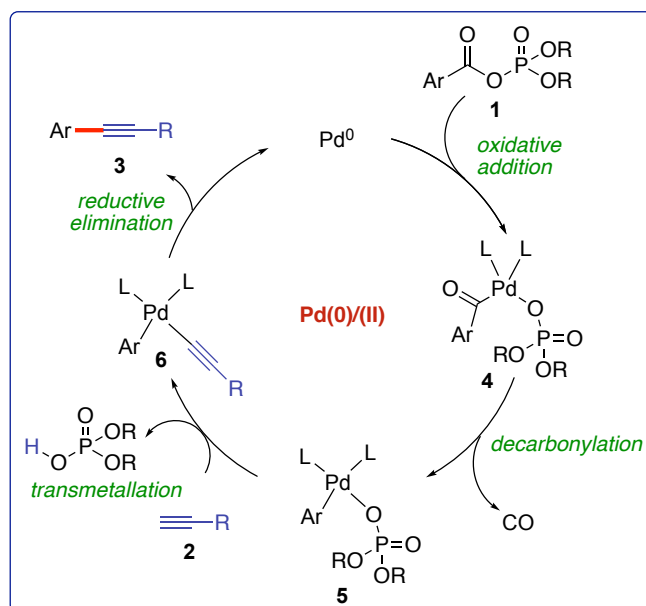
(Scheme 4C). This should be because substrates with certain steric hindrance are more conducive to reductive elimination. Furthermore, electron-deficient carboxylic–phosphoric anhydrides were more reactive than their electron-rich counterparts (Scheme 4D). This may be due to that substrates with electron-withdrawing groups have stronger electrophilicity, resulting them more favorable for oxidative addition. The high reactivity of carboxylic–phosphoric anhydrides underscores the potential of this class of substrates in decarbonylative cross-coupling protocols.

Scheme 4. Competition Experiments



The proposed reaction mechanism was shown in Scheme 5. As shown, palladium first inserts the C(O)–O bond of carboxylic–phosphoric anhydride to form intermediate **4** via oxidative addition. Next, intermediate **4** is converted to intermediate **5** via decarbonylation. Subsequently, transmetallation between terminal alkynes **2** and intermediate **5** generates aryl–Pd complex **6**. Finally, the internal alkyne product and zero valent palladium are obtained through reductive elimination.

Scheme 5. Proposed Mechanism



Conclusions

In summary, we have reported the first decarbonylative alkynylation of carboxylic-phosphoric anhydrides via highly selective C(O)–O bond cleavage vs. P(O)–O bond cleavage using palladium catalysis. This method enables to convert ubiquitous carboxylic acids through orthogonal activation with phosphates or phosphites to give carboxylic-phosphoric anhydrides, which have been shown to be among the most reactive carboxylic acid derivatives for decarbonylative coupling. Highly valuable internal alkynes have been synthesized by this robust decarbonylative alkynylation, and the utility has been demonstrated by excellent functional group tolerance and broad substrate scope. More generally, the high reactivity of carboxylic-phosphoric anhydrides and excellent selectivity of C(O)–O bond cleavage vs. P(O)–O bond cleavage bodes well for the future use of this class of electrophiles in a plethora of highly valuable decarbonylative processes.

Experimental Section

General Methods. All reactions were carried out under an inert atmosphere of argon in oven-dried sealed microwave tube vials using standard techniques for handling air-sensitive reagents. All reagents

were purchased and used as received from a supplier unless otherwise noted. A Bruker 400 MHz spectrometer was used for NMR spectra generation.

General Procedure A for the Synthesis of Carboxylic-Phosphoric Anhydrides.¹⁸ An oven-dried flask (50 mL) equipped with a stir bar was charged with acyl chlorides (typically, 10.0 mmol, 1.0 equiv), hydrogen phosphates (2.2 equiv), silver oxide (1.0 equiv) in acetonitrile (20 mL). The reaction mixture was stirred for 15 h at room temperature. After the indicated time, the reaction mixture was filtrated, washed with water (30 mL) and CH₂Cl₂ (30 mL), dried, filtrated, concentrated to get crude product. Unless stated otherwise, the crude product was purified by chromatography (ethyl acetate/hexane = 1/10 to 1/2) to give analytically pure product.

General Procedure B for the Synthesis of Carboxylic-Phosphoric Anhydrides.¹⁹ An oven-dried flask (50 mL) equipped with a stir bar was charged with carboxylic acids (typically, 10.0 mmol, 1.0 equiv), phosphites (3.0 equiv), Cu₂O (0.1 equiv), dicumyl peroxide (4.0 equiv) and acetonitrile (30 mL). The mixture was allowed to stir at 70 °C for 12 h under air atmosphere. Upon completion as shown by TLC, the reaction mixture was cooled to room temperature. After the indicated time, the reaction mixture was diluted with acetonitrile (30 mL), filtrated, concentrated to get crude product. Unless stated otherwise, the crude product was purified by chromatography (ethyl acetate/hexane = 1/10 to 1/2) to give analytically pure product.

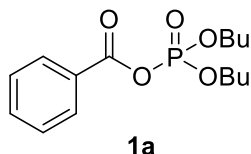
General Procedure for Palladium-Catalyzed Decarbonylative Alkynylation of Carboxylic-Phosphoric Anhydrides. An oven-dried vial equipped with a stir bar was charged with carboxylic-phosphoric anhydrides (neat, 1.0 equiv), alkynes (neat, 3.0 equiv), Pd(OAc)₂ (typically, 5 mol %), XantPhos (typically, 10 mol %), and Et₃N (1.5 equiv), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. Dioxane (typically, 0.20 M) was added with vigorous stirring at room temperature, and the reaction mixture was placed in a preheated oil bath at 160 °C and stirred for 15 h at 160 °C. After the indicated time, the reaction mixture was cooled down to room temperature. The sample was analyzed by ¹H NMR (CDCl₃, 400 MHz) and GC-MS to

obtain conversion, yield and selectivity using internal standard and comparison with authentic samples. Purification by chromatography on silica gel (hexane/dichloromethane) afforded the title product. Caution: reactions involving high pressure must be carried out in a well-ventilated hood with appropriate pressure vessels, pressure relief equipment, and/or blast shields.

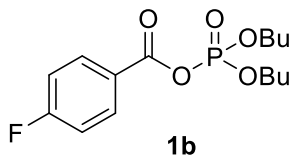
Representative Procedure for Palladium-Catalyzed Decarbonylative Alkynylation of Carboxylic-Phosphoric Anhydrides. An oven-dried vial equipped with a stir bar was charged with benzoic (dibutyl phosphoric) anhydride (neat, 62.8 mg, 0.20 mmol, 1.0 equiv), 1-ethynyl-4-methoxybenzene (79.3 mg, 0.6 mmol, 3.0 equiv), Pd(OAc)₂ (2.2 mg, 0.01 mmol, 5 mol %), XantPhos (11.6 mg, 0.02 mmol, 10 mol %) and Et₃N (neat, 30.4 mg, 0.3 mmol, 1.5 equiv), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. Dioxane (1.0 mL, 0.20 M) was added with vigorous stirring at room temperature, and the reaction mixture was placed in a preheated oil bath at 160 °C and stirred for 15 h at 160 °C. After the indicated time, the reaction mixture was cooled down to room temperature. Purification by chromatography on silica gel (hexanes/dichloromethane) afforded the title product. Yield 71% (29.6 mg, 0.14 mmol). White solid. Characterization data are included in the section below.

Large Scale Example for Palladium-Catalyzed Decarbonylative Alkynylation of Carboxylic-Phosphoric Anhydrides. An oven-dried vial equipped with a stir bar was charged with benzoic (dibutyl phosphoric) anhydride (neat, 1.0 g, 3.18 mmol, 1.0 equiv), 1-ethynyl-4-methoxybenzene (1.26 g, 9.54 mmol, 3.0 equiv), Pd(OAc)₂ (35.7 mg, 0.16 mmol, 5 mol %), XantPhos (184.0 mg, 0.318 mmol, 10 mol %) and Et₃N (neat, 482.7 mg, 4.77 mmol, 1.5 equiv), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. Dioxane (16.0 mL, 0.20 M) was added with vigorous stirring at room temperature, and the reaction mixture was placed in a preheated oil bath at 160 °C and stirred for 15 h at 160 °C. After the indicated time, the reaction mixture was cooled down to room temperature. After the indicated time, the reaction mixture was cooled down to room temperature. Purification by chromatography on silica gel (hexane/dichloromethane = 10/1 to 1/1)

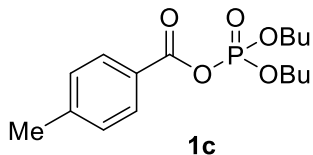
afforded the title product. Isolated yield 74% (490.1 mg, 2.35 mmol). White solid. Characterization data are included in the section below.



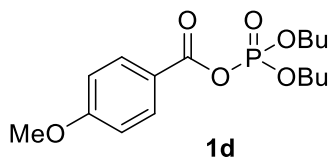
Benzoic (dibutyl phosphoric) anhydride (1a).²⁰ This compound was synthesized using procedure A. Yield 83% (2.609 g). Colorless oil. **¹H NMR (400 MHz, CDCl₃)** δ 8.06-8.04 (m, *J* = 8.4, 1.3 Hz, 2H), 7.66-7.62 (m, 1H), 7.50-7.46 (m, 2H), 4.32-4.26 (m, *J* = 6.6, 1.6 Hz, 4H), 1.76-1.69 (m, 4H), 1.49-1.40 (m, 4H), 0.94 (t, *J* = 7.4 Hz, 6H). **¹³C{¹H} NMR (101 MHz, CDCl₃)** δ 161.0 (d, *J* = 8.3 Hz), 134.4, 130.6, 128.7, 128.2 (d, *J* = 8.4 Hz), 69.0 (d, *J* = 6.1 Hz), 32.2 (d, *J* = 6.9 Hz), 18.6, 13.5. **³¹P NMR (162 MHz, CDCl₃)** δ -6.80.



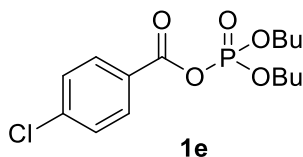
(Dibutyl phosphoric) 4-fluorobenzoic anhydride (1b). This compound was synthesized using procedure A. Yield 78% (2.592 g). *New compound*. Colorless oil. **¹H NMR (400 MHz, CDCl₃)** δ 8.08-8.05 (m, 2H), 7.15 (t, *J* = 8.6 Hz, 2H), 4.33-4.23 (m, *J* = 6.7, 2.3 Hz, 4H), 1.74-1.69 (m, 4H), 1.49-1.39 (m, 4H), 0.94 (t, *J* = 7.4 Hz, 6H). **¹³C{¹H} NMR (101 MHz, CDCl₃)** δ 167.9, 165.4, 133.4 (d, *J* = 9.7 Hz), 124.5 (d, *J* = 8.6, 2.8 Hz), 116.1 (d, *J* = 22.4 Hz), 69.0 (d, *J* = 6.1 Hz), 32.2 (d, *J* = 6.9 Hz), 18.6, 13.5. **³¹P NMR (162 MHz, CDCl₃)** δ -6.87. **¹⁹F NMR (376 MHz, CDCl₃)** δ -102.32. **HMRS** calcd for C₁₅H₂₂FO₅P (M⁺ + H) 333.1267, found 333.1285.



(Dibutyl phosphoric) 4-methylbenzoic anhydride (1c).²¹ This compound was synthesized using procedure A. Yield 90% (2.955 g). Colorless oil. **¹H NMR (400 MHz, CDCl₃)** δ 7.93 (d, *J* = 7.8 Hz, 2H), 7.27 (d, *J* = 8.2 Hz, 2H), 4.31-4.25 (m, 4H), 2.43 (s, 3H), 1.76-1.69 (m, 4H), 1.49-1.40 (m, 4H), 0.94 (t, *J* = 7.3 Hz, 6H). **¹³C{¹H} NMR (101 MHz, CDCl₃)** δ 161.0 (d, *J* = 8.2 Hz), 145.6, 130.7, 129.5, 125.4 (d, *J* = 8.4 Hz), 68.9 (d, *J* = 6.1 Hz), 32.2 (d, *J* = 6.9 Hz), 21.8, 18.6, 13.5. **³¹P NMR (162 MHz, CDCl₃)** δ -6.74.

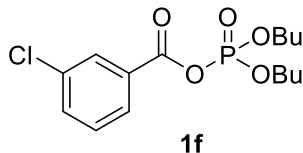


(Dibutyl phosphoric) 4-methoxybenzoic anhydride (1d). This compound was synthesized using procedure A. Yield 82% (2.823 g). New compound. Colorless oil. **¹H NMR (400 MHz, CDCl₃)** δ 8.00 (d, *J* = 8.9 Hz, 2H), 6.95-6.93 (m, 2H), 4.31-4.24 (m, 4H), 3.88 (s, 3H), 1.76-1.67 (m, 4H), 1.49-1.40 (m, 4H), 0.94 (t, *J* = 7.4 Hz, 6H). **¹³C{¹H} NMR (101 MHz, CDCl₃)** δ 164.6, 160.6 (d, *J* = 8.5 Hz), 132.9, 120.3 (d, *J* = 8.6 Hz), 114.0, 68.9 (d, *J* = 6.2 Hz), 55.6, 32.2 (d, *J* = 7.0 Hz), 18.6, 13.6. **³¹P NMR (162 MHz, CDCl₃)** δ -6.70. **HMRS** calcd for C₁₆H₂₅O₆P (M⁺ + H) 345.1467, found 345.1484.

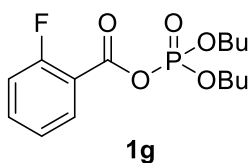


(Dibutyl phosphoric) 4-chlorobenzoic anhydride (1e). This compound was synthesized using procedure A. Yield 81% (2.825 g). New compound. Colorless oil. **¹H NMR (400 MHz, CDCl₃)** δ 8.09-8.05 (m, 2H), 7.15 (t, *J* = 8.7 Hz, 2H), 4.31-4.25 (m, 4H), 1.76-1.69 (m, 4H), 1.49-1.39 (m, 4H), 0.94 (t,

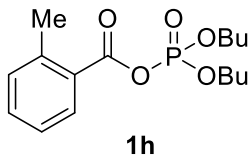
$J = 7.5$ Hz, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 167.9, 165.3, 133.4 (d, $J = 9.7$ Hz), 124.5 (d, $J = 10.2$ Hz), 116.1 (d, $J = 22.2$ Hz), 69.1 (d, $J = 6.1$ Hz), 32.2 (d, $J = 6.9$ Hz), 18.6, 13.5. ^{31}P NMR (162 MHz, CDCl_3) δ -6.87. **HMRS** calcd for $\text{C}_{15}\text{H}_{22}\text{ClO}_5\text{P}$ ($\text{M}^+ + \text{H}$) 349.0972, found 349.0975.



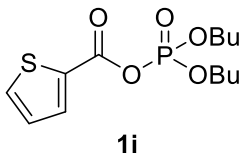
(Dibutyl phosphoric) 3-chlorobenzoic anhydride (1f). This compound was synthesized using procedure A. Yield 75% (2.616 g). *New compound.* Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 8.01 (s, 1H), 7.93 (d, $J = 7.8$ Hz, 1H), 7.61 (d, $J = 8.0$ Hz, 1H), 7.43 (t, $J = 7.9$ Hz, 1H), 4.31-4.26 (m, 4H), 1.76-1.69 (m, 4H), 1.49-1.40 (m, 4H), 0.95 (t, $J = 7.4$ Hz, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 160.0, 159.9, 135.0, 134.5, 130.5, 130.1 (d, $J = 3.8$ Hz), 128.7, 69.2 (d, $J = 6.2$ Hz), 32.2 (d, $J = 6.8$ Hz), 18.6, 13.5. ^{31}P NMR (162 MHz, CDCl_3) δ -6.99. **HMRS** calcd for $\text{C}_{15}\text{H}_{22}\text{ClO}_5\text{P}$ ($\text{M}^+ + \text{H}$) 349.0972, found 349.0983.



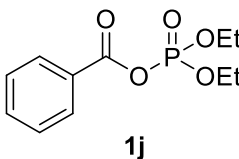
(Dibutyl phosphoric) 2-fluorobenzoic anhydride (1g). This compound was synthesized using procedure A. Yield 79% (2.625 g). *New compound.* Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 8.00-7.95 (m, 1H), 7.64-7.58 (m, 1H), 7.27-7.22 (m, 1H), 7.20-7.15 (m, 1H), 4.34-4.23 (m, 4H), 1.76-1.68 (m, 4H), 1.48-1.39 (m, 4H), 0.94 (t, $J = 7.4$ Hz, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 163.9, 161.2, 136.3 (d, $J = 9.4$ Hz), 133.0, 124.3 (d, $J = 3.9$ Hz), 117.3 (d, $J = 22.1$ Hz), 116.7 (t, $J = 8.5$ Hz), 69.1 (d, $J = 6.2$ Hz), 32.1 (d, $J = 7.1$ Hz), 18.6, 13.5. ^{31}P NMR (162 MHz, CDCl_3) δ -7.53. ^{19}F NMR (376 MHz, CDCl_3) δ -108.30. **HMRS** calcd for $\text{C}_{15}\text{H}_{22}\text{FO}_5\text{P}$ ($\text{M}^+ + \text{H}$) 333.1267, found 333.1268.



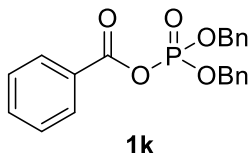
(Dibutyl phosphoric) 2-methylbenzoic anhydride (1h). This compound was synthesized using procedure A. Yield 77% (2.528 g). *New compound.* Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.99 - 7.97 (m, 1H), 7.51-7.45 (m, 1H), 7.3 (d, J = 7.6 Hz, 2H), 4.31-4.26 (m, 4H), 2.64 (s, 3H), 1.76-1.69 (m, 4H), 1.49-1.40 (m, 4H), 0.95 (t, J = 7.4 Hz, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 161.0 (d, J = 8.5 Hz), 142.7, 133.7, 132.2, 131.8, 126.8 (d, J = 7.8 Hz), 126.0, 68.9 (d, J = 6.1 Hz), 32.2 (d, J = 6.9 Hz), 22.1, 18.6, 13.6. ^{31}P NMR (162 MHz, CDCl_3) δ -6.75. **HMRS** calcd for $\text{C}_{16}\text{H}_{25}\text{O}_5\text{P}$ ($\text{M}^+ + \text{H}$) 329.1518, found 329.1526.



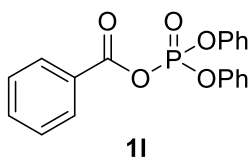
(Dibutyl phosphoric) thiophene-2-carboxylic anhydride (1i). This compound was synthesized using procedure A. Yield 87% (2.787 g). *New compound.* Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.89-7.88 (m, J = 3.9, 1.3 Hz, 1H), 7.70-7.69 (m, J = 4.9, 1.3 Hz, 1H), 7.16-7.14 (m, J = 5.0, 3.8 Hz, 1H), 4.30-4.24 (m, 4H), 1.76-1.68 (m, 4H), 1.49-1.39 (m, J = 14.8, 7.4 Hz, 4H), 0.94 (t, J = 7.4 Hz, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 156.0 (d, J = 7.5 Hz), 136.1, 135.2, 131.6 (d, J = 9.9 Hz), 128.4, 69.1 (d, J = 6.2 Hz), 32.1 (d, J = 6.9 Hz), 18.6, 13.5. ^{31}P NMR (162 MHz, CDCl_3) δ -7.58. **HMRS** calcd for $\text{C}_{13}\text{H}_{21}\text{O}_5\text{PS}$ ($\text{M}^+ + \text{H}$) 321.0926, found 321.0931.



Benzoic (diethyl phosphoric) anhydride (1j).²² This compound was synthesized using procedure B. Yield 82% (2.112 g). Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 8.07-8.05 (m, *J* = 8.3, 1.1 Hz, 2H), 7.67-7.63 (m, 1H), 7.49 (t, *J* = 7.8 Hz, 2H), 4.41-4.33 (m, *J* = 7.2 Hz, 4H), 1.44-1.40 (m, 6H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 161.0 (d, *J* = 8.2 Hz), 134.5, 130.6, 128.7, 128.1 (d, *J* = 8.2 Hz), 65.3 (d, *J* = 5.8 Hz), 16.1 (d, *J* = 6.9 Hz). ³¹P NMR (162 MHz, CDCl₃) δ -7.06.



Benzoic (dibenzyl phosphoric) anhydride (1k).²³ This compound was synthesized using procedure A. Yield 72% (2.753 g). White solid. ¹H NMR (400 MHz, CDCl₃) δ 7.88-7.85 (m, 2H), 7.64-7.60 (m, 1H), 7.45-7.33 (m, 12H), 5.29 (d, *J* = 8.9 Hz, 4H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 160.9 (d, *J* = 8.4 Hz), 135.26 (d, *J* = 6.7 Hz), 134.5, 131.7, 130.7, 128.7 (d, *J* = 7.3 Hz), 128.2, 127.9, 127.8, 70.5 (d, *J* = 5.6 Hz). ³¹P NMR (162 MHz, CDCl₃) δ -6.69.



Benzoic (diphenyl phosphoric) anhydride (1l).²⁴ This compound was synthesized using procedure A. Yield 80% (2.834 g). Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 8.04-8.01 (m, 2H), 7.68-7.64 (m, 1H), 7.50-7.46 (m, 2H), 7.40-7.32 (m, 8H), 7.24-7.20 (m, 2H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 171.9, 150.4 (d, *J* = 7.0 Hz), 133.8, 130.2, 129.7 (d, *J* = 0.8 Hz), 129.3, 128.5, 125.4, 120.2 (d, *J* = 4.9 Hz). ³¹P NMR (162 MHz, CDCl₃) δ -9.11.

1,2-Diphenylethyne (Scheme 1, 3a).²⁵ According to the general procedure, the reaction of benzoic (dibutyl phosphoric) anhydride (0.2 mmol, 1.0 equiv), ethynylbenzene (0.6 mmol, 3.0 equiv), Pd(OAc)₂

(0.01 mmol, 5 mol %), XantPhos (0.02 mmol, 10 mol %) and Et₃N (0.3 mmol, 1.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography (hexane/dichloromethane = 10/1 to 1/1) the title compound in 56% yield (19.8 mg). White solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.55-7.53 (m, 4H), 7.36-7.34 (m, 6H). **¹³C{¹H} NMR (101 MHz, CDCl₃)** δ 131.7, 128.4, 128.3, 123.4, 89.4.

1-Methyl-4-(phenylethynyl)benzene (Scheme 1, 3b).²⁵ According to the general procedure, the reaction of benzoic (dibutyl phosphoric) anhydride (0.2 mmol, 1.0 equiv), 1-ethynyl-4-methylbenzene (0.6 mmol, 3.0 equiv), Pd(OAc)₂ (0.01 mmol, 5 mol %), XantPhos (0.02 mmol, 10 mol %) and Et₃N (0.3 mmol, 1.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography (hexane/dichloromethane = 10/1 to 1/1) the title compound in 82% yield (31.6 mg). Yellow solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.53 (d, *J* = 7.4 Hz, 2H), 7.43 (d, *J* = 7.9 Hz, 2H), 7.34 (d, *J* = 6.2 Hz, 3H), 7.16 (d, *J* = 7.8 Hz, 2H), 2.37 (s, 3H). **¹³C{¹H} NMR (101 MHz, CDCl₃)** δ 138.4, 131.5, 131.5, 129.1, 128.3, 128.1, 123.5, 120.2, 89.5, 88.7, 21.5.

1-Methoxy-4-(phenylethynyl)benzene (Scheme 1, 3c).²⁵ According to the general procedure, the reaction of benzoic (dibutyl phosphoric) anhydride (0.2 mmol, 1.0 equiv), 1-ethynyl-4-methoxybenzene (0.6 mmol, 3.0 equiv), Pd(OAc)₂ (0.01 mmol, 5 mol %), XantPhos (0.02 mmol, 10 mol %) and Et₃N (0.3 mmol, 1.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography (hexane/dichloromethane = 10/1 to 1/1) the title compound in 71% yield (29.6 mg). White solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.52-7.46 (m, 4H), 7.35-7.32 (m, 3H), 6.88 (d, *J* = 8.7 Hz, 2H), 3.83 (s, 3H). **¹³C{¹H} NMR (101 MHz, CDCl₃)** δ 159.6, 133.0, 131.4, 128.3, 127.9, 123.6, 115.4, 114.0, 89.3, 88.0, 55.3.

1-(Phenylethynyl)-4-(trifluoromethyl)benzene (Scheme 1, 3d).²⁶ According to the general procedure, the reaction of benzoic (dibutyl phosphoric) anhydride (0.2 mmol, 1.0 equiv), 1-ethynyl-4-

(trifluoromethyl)benzene (0.6 mmol, 3.0 equiv), Pd(OAc)₂ (0.01 mmol, 5 mol %), XantPhos (0.02 mmol, 10 mol %) and Et₃N (0.3 mmol, 1.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography (hexane/dichloromethane = 10/1 to 1/1) the title compound in 90% yield (24.4 mg). White solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.65-7.60 (m, 4H), 7.57-7.54 (m, 2H), 7.38-7.36 (m, 3H). **¹³C{¹H} NMR (101 MHz, CDCl₃)** δ 131.8, 131.7, 130.0, 129.7, 128.8, 128.4, 127.1 (q, *J*^F = 2.0 Hz), 125.3 (q, *J*^F = 4.0 Hz), 122.5, 91.7, 87.9. **¹⁹F NMR (376 MHz, CDCl₃)** δ -62.66.

1-Fluoro-4-(phenylethynyl)benzene (Scheme 1, 3e).²⁷ According to the general procedure, the reaction of benzoic (dibutyl phosphoric) anhydride (0.2 mmol, 1.0 equiv), 1-ethynyl-4-fluorobenzene (3.0 equiv), Pd(OAc)₂ (0.6 mmol, 3.0 equiv), Pd(OAc)₂ (0.01 mmol, 5 mol %), XantPhos (0.02 mmol, 10 mol %) and Et₃N (0.3 mmol, 1.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography (hexane/dichloromethane = 10/1 to 1/1) the title compound in 84% yield (33.6 mg). White solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.54-7.51(m, 4H), 7.36-7.33 (m, 3H), 7.05 (t, *J* = 8.0 Hz, 2H). **¹³C{¹H} NMR (101 MHz, CDCl₃)** δ 163.5 (d, *J*^F = 64.5 Hz), 138.3, 133.6 (d, *J*^F = 8.3 Hz), 131.6, 129.8, 128.4 (d, *J*^F = 3.8 Hz), 123.2, 119.4 (d, *J*^F = 3.4 Hz), 115.7 (d, *J*^F = 22.0 Hz), 89.1, 88.4. **¹⁹F NMR (376 MHz, CDCl₃)** δ -110.89.

1-Chloro-4-(phenylethynyl)benzene (Scheme 1, 3f).²⁵ According to the general procedure, the reaction of benzoic (dibutyl phosphoric) anhydride (0.2 mmol, 1.0 equiv), 1-chloro-4-ethynylbenzene (0.6 mmol, 3.0 equiv), Pd(OAc)₂ (0.01 mmol, 5 mol %), XantPhos (0.02 mmol, 10 mol %) and Et₃N (0.3 mmol, 1.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography (hexane/dichloromethane = 10/1 to 1/1) the title compound in 61% yield (26.0 mg). Yellow solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.53-7.51 (m, 2H), 7.46 (d, *J* = 7.2 Hz, 2H), 7.36-7.32 (m, 5H). **¹³C{¹H} NMR (101 MHz, CDCl₃)** δ 134.3, 132.9, 131.7, 128.8, 128.6, 128.5, 123.0, 121.9, 90.4, 88.3.

Methyl 4-(phenylethynyl)benzoate (Scheme 1, 3g).²⁵ According to the general procedure, the reaction of benzoic (dibutyl phosphoric) anhydride (0.2 mmol, 1.0 equiv), methyl 4-ethynylbenzoate (0.6 mmol, 3.0 equiv), Pd(OAc)₂ (0.01 mmol, 5 mol %), XantPhos (0.02 mmol, 10 mol %) and Et₃N (0.3 mmol, 1.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography (hexane/dichloromethane = 10/1 to 1/1) the title compound in 81% yield (38.2 mg). Yellow solid. ¹H NMR (400 MHz, CDCl₃) δ 8.02 (d, *J* = 8.4 Hz, 2H), 7.60-7.52 (m, 4H), 7.38-7.36 (m, 3H), 3.93 (s, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 166.7, 131.8, 131.6, 129.6, 129.5, 128.9, 128.5, 128.1, 122.8, 92.4, 88.7, 52.3.

1-Fluoro-2-(phenylethynyl)benzene (Scheme 1, 3h).²⁵ According to the general procedure, the reaction of benzoic (dibutyl phosphoric) anhydride (0.2 mmol, 1.0 equiv), 1-ethynyl-2-fluorobenzene (0.6 mmol, 3.0 equiv), Pd(OAc)₂ (0.01 mmol, 5 mol %), XantPhos (0.02 mmol, 10 mol %) and Et₃N (0.3 mmol, 1.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography (hexane/dichloromethane = 10/1 to 1/1) the title compound in 87% yield (34.2 mg). White solid. ¹H NMR (400 MHz, CDCl₃) δ 7.58-7.50 (m, 3H), 7.37-7.29 (m, 4H), 7.15-7.09 (m, 2H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 162.6 (d, *J*^F = 251.8 Hz), 133.4 (d, *J*^F = 1.0 Hz), 131.7, 129.9 (d, *J*^F = 7.8 Hz), 128.6, 128.4, 123.9 (d, *J*^F = 3.8 Hz), 122.9, 115.5 (d, *J*^F = 21.0 Hz), 111.9 (d, *J*^F = 15.6 Hz), 94.4, 82.6. ¹⁹F NMR (376 MHz, CDCl₃) δ -109.78.

1-Chloro-2-(phenylethynyl)benzene (Scheme 1, 3i).²⁷ According to the general procedure, the reaction of benzoic (dibutyl phosphoric) anhydride (0.2 mmol, 1.0 equiv), 1-chloro-2-ethynylbenzene (0.6 mmol, 3.0 equiv), Pd(OAc)₂ (0.01 mmol, 5 mol %), XantPhos (0.02 mmol, 10 mol %) and Et₃N (0.3 mmol, 1.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography (hexane/dichloromethane = 10/1 to 1/1) the title compound in 57% yield (24.2 mg). Yellow solid. ¹H NMR (400 MHz, CDCl₃) δ 7.59-7.56 (m, 3H), 7.43 (d, *J* = 8.1 Hz, 1H), 7.37 (d, *J* = 3.8 Hz, 3H), 7.25

(s, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 135.9, 133.2, 131.7, 129.3, 129.2, 128.6, 128.4, 126.4, 123.2, 122.9, 94.5, 86.1.

((4-Fluorophenyl)ethynyl)triisopropylsilane (Scheme 1, 3j).²⁸ According to the general procedure, the reaction of (dibutyl phosphoric) 4-fluorobenzoic anhydride (0.2 mmol, 1.0 equiv), ethynyltriisopropylsilane (0.6 mmol, 3.0 equiv), $\text{Pd}(\text{OAc})_2$ (0.01 mmol, 5 mol %), XantPhos (0.02 mmol, 10 mol %) and Et_3N (0.3 mmol, 1.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography (hexane/dichloromethane = 10/1 to 1/1) the title compound in 70% yield (38.6 mg). Yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.47-7.43 (m, 2H), 6.99 (t, J = 8.7 Hz, 2H), 1.12 (s, 21H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 163.7, 133.9 (d, J^F = 8.3 Hz), 119.7, 115.4 (d, J^F = 22.1 Hz), 93.7, 90.2, 18.6, 11.3. ^{19}F NMR (376 MHz, CDCl_3) δ -110.72.

1-Methyl-4-(phenylethynyl)benzene (Scheme 1, 3b').²⁵ According to the general procedure, the reaction of (dibutyl phosphoric) 4-methylbenzoic anhydride (0.2 mmol, 1.0 equiv), 1-ethynyl-4-methylbenzene (0.6 mmol, 3.0 equiv), $\text{Pd}(\text{OAc})_2$ (0.01 mmol, 5 mol %), XantPhos (0.02 mmol, 10 mol %) and Et_3N (0.3 mmol, 1.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography (hexane/dichloromethane = 10/1 to 1/1) the title compound in 82% yield (31.6 mg). Yellow solid. ^1H NMR (400 MHz, CDCl_3) δ 7.53 (d, J = 7.4 Hz, 2H), 7.43 (d, J = 7.9 Hz, 2H), 7.34 (d, J = 6.2 Hz, 3H), 7.16 (d, J = 7.8 Hz, 2H), 2.37 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 138.4, 131.5, 131.5, 129.1, 128.3, 128.1, 123.5, 120.2, 89.5, 88.7, 21.5.

1-Methoxy-4-(phenylethynyl)benzene (Scheme 1, 3c').²⁵ According to the general procedure, the reaction of (dibutyl phosphoric) 4-methoxybenzoic anhydride (0.2 mmol, 1.0 equiv), 1-ethynyl-4-methoxybenzene (0.6 mmol, 3.0 equiv), $\text{Pd}(\text{OAc})_2$ (0.01 mmol, 5 mol %), XantPhos (0.02 mmol, 10 mol %) and Et_3N (0.3 mmol, 1.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography (hexane/dichloromethane = 10/1 to 1/1) the title compound in 71% yield (29.6

mg). White solid. **¹H NMR (400 MHz, CDCl₃)** 7.52-7.46 (m, 4H), 7.35-7.32 (m, 3H), 6.88 (d, *J* = 8.7 Hz, 2H), 3.83 (s, 3H). **¹³C{¹H} NMR (101 MHz, CDCl₃)** δ 159.6, 133.0, 131.4, 128.3, 127.9, 123.6, 115.4, 114.0, 89.3, 88.0, 55.3.

1-Fluoro-4-(phenylethynyl)benzene (Scheme 1, 3e').²⁷ According to the general procedure, the reaction of (dibutyl phosphoric) 4-fluorobenzoic anhydride (0.2 mmol, 1.0 equiv), ethynylbenzene (0.6 mmol, 3.0 equiv), Pd(OAc)₂ (0.01 mmol, 5 mol %), XantPhos (0.02 mmol, 10 mol %) and Et₃N (0.3 mmol, 1.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography (hexane/dichloromethane = 10/1 to 1/1) the title compound in 88% yield (34.6 mg). White solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.54-7.51(m, 4H), 7.36-7.33 (m, 3H), 7.05 (t, *J* = 8.0 Hz, 2H). **¹³C{¹H} NMR (101 MHz, CDCl₃)** δ 163.5 (d, *J^F* = 64.5 Hz), 138.3, 133.6 (d, *J^F* = 8.3 Hz), 131.6, 129.8, 128.4 (d, *J^F* = 3.8 Hz), 123.2, 119.4 (d, *J^F* = 3.4 Hz), 115.7 (d, *J^F* = 22.0 Hz), 89.1, 88.4. **¹⁹F NMR (376 MHz, CDCl₃)** δ -110.89.

1-Chloro-4-((4-methoxyphenyl)ethynyl)benzene (Scheme 1, 3k).²⁷ According to the general procedure, the reaction of (dibutyl phosphoric) 4-chlorobenzoic anhydride (0.2 mmol, 1.0 equiv), 1-ethynyl-4-methoxybenzene (0.6 mmol, 3.0 equiv), Pd(OAc)₂ (0.01 mmol, 5 mol%), XantPhos (0.02 mmol, 10 mol %) and Et₃N (0.3 mmol, 1.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography (hexane/dichloromethane = 10/1 to 1/1) the title compound in 67% yield (32.6 mg). White solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.52-7.45 (m, 4H), 7.33 (d, *J* = 6.6 Hz, 1H), 7.03 (t, *J* = 8.5 Hz, 1H), 6.88 (d, *J* = 7.9 Hz, 2H), 3.83 (s, 3H). **¹³C{¹H} NMR (101 MHz, CDCl₃)** δ 159.6, 133.3, 133.0, 131.4, 128.3, 123.6, 115.5, 114.0, 90.1, 88.0, 55.3.

1-Chloro-3-((4-methoxyphenyl)ethynyl)benzene (Scheme 1, 3l).²⁷ According to the general procedure, the reaction of (dibutyl phosphoric) 3-chlorobenzoic anhydride (0.2 mmol, 1.0 equiv), 1-ethynyl-4-methoxybenzene (0.6 mmol, 3.0 equiv), Pd(OAc)₂ (0.01 mmol, 5 mol %), XantPhos (0.02 mmol, 10

mol %) and Et₃N (0.3 mmol, 1.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography (hexane/dichloromethane = 10/1 to 1/1) the title compound in 75% yield (36.4 mg). White solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.53-7.45 (m, 3H), 7.40-7.37 (m, 1H), 7.34-7.28 (m, 2H), 6.90-6.87 (m, 2H), 3.84 (s, 3H). **¹³C{¹H} NMR (101 MHz, CDCl₃)** δ 159.7, 133.1, 131.3, 129.5, 129.5, 128.3, 128.3, 114.1, 114.0, 90.6, 86.7, 55.3.

1-Fluoro-2-((4-methoxyphenyl)ethynyl)benzene (Scheme 1, 3m).²⁷ According to the general procedure, the reaction of (dibutyl phosphoric) 2-fluorobenzoic anhydride (0.2 mmol, 1.0 equiv), 1-ethynyl-4-methoxybenzene (0.6 mmol, 3.0 equiv), Pd(OAc)₂ (0.01 mmol, 5 mol %), XantPhos (0.02 mmol, 10 mol %) and Et₃N (0.3 mmol, 1.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography (hexane/dichloromethane = 10/1 to 1/1) the title compound in 84% yield (38.0 mg). White solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.52-7.46 (m, 3H), 7.34-7.27 (m, 1H), 7.17-7.11 (m, 2H), 6.89 (d, *J* = 8.7 Hz, 2H), 3.83 (s, 3H). **¹³C{¹H} NMR (101 MHz, CDCl₃)** δ 163.7 (d, *J^F* = 15.0 Hz), 159.8, 133.3 (d, *J^F* = 1.4 Hz), 133.2, 129.6 (d, *J^F* = 7.9 Hz), 123.9 (d, *J^F* = 3.7 Hz), 115.5 (d, *J^F* = 20.9 Hz), 115.0, 114.0, 112.2 (d, *J^F* = 15.8 Hz), 94.5, 88.0, 55.3. **¹⁹F NMR (376 MHz, CDCl₃)** δ -109.78.

1-Methyl-2-(phenylethynyl)benzene (Scheme 1, 3n).²⁵ According to the general procedure, the reaction of (dibutyl phosphoric) 2-methylbenzoic anhydride (0.2 mmol, 1.0 equiv), ethynylbenzene (0.6 mmol, 3.0 equiv), Pd(OAc)₂ (0.01 mmol, 5 mol %), XantPhos (0.02 mmol, 10 mol %) and Et₃N (0.3 mmol, 1.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography (hexane/dichloromethane = 10/1 to 1/1) the title compound in 46% yield (35.2 mg). Yellow solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.55-7.49 (m, 3H), 7.36-7.34 (m, 3H), 7.24 (d, *J* = 3.8 Hz, 2H), 7.19-7.15 (m, 1H), 2.52 (s, 3H). **¹³C{¹H} NMR (101 MHz, CDCl₃)** δ 140.2, 131.8, 131.5, 129.4, 128.3, 128.3, 128.2, 125.6, 123.5, 123.0, 93.3, 88.3, 20.7.

2-((4-Methoxyphenyl)ethynyl)thiophene (Scheme 1, 3o).²⁸ According to the general procedure, the reaction of (dibutyl phosphoric) thiophene-2-carboxylic anhydride (0.2 mmol, 1.0 equiv), 1-ethynyl-4-methoxybenzene (0.6 mmol, 3.0 equiv), Pd(OAc)₂ (0.01 mmol, 5 mol %), XantPhos (0.02 mmol, 10 mol %) and Et₃N (0.3 mmol, 1.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography (hexane/dichloromethane = 10/1 to 1/1) the title compound in 88% yield (37.7 mg). Yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.53-7.44 (m, 3H), 7.33 (d, *J* = 6.8 Hz, 1H), 7.00 (t, *J* = 4.3 Hz, 1H), 6.88 (d, *J* = 8.0 Hz, 2H), 3.83 (s, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 159.7, 133.0, 131.4, 127.0, 126.8, 123.7, 115.0, 114.0, 93.0, 81.2, 55.3.

1,2-Diphenylethyne from benzoic (diethyl phosphoric) anhydride and ethynylbenzene (Scheme 2, 3a).²⁵ According to the general procedure, the reaction of benzoic (diethyl phosphoric) anhydride (0.2 mmol, 1.0 equiv), ethynylbenzene (0.6 mmol, 3.0 equiv), Pd(OAc)₂ (0.01 mmol, 5 mol %), XantPhos (0.02 mmol, 10 mol %) and Et₃N (0.3 mmol, 1.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography (hexane/dichloromethane = 10/1 to 1/1) the title compound in 92% yield (32.8 mg). White solid. ¹H NMR (400 MHz, CDCl₃) δ 7.55-7.53 (m, 4H), 7.36-7.34 (m, 6H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 131.7, 128.4, 128.3, 123.4, 89.4.

1,2-Diphenylethyne from benzoic (dibenzyl phosphoric) anhydride and ethynylbenzene (Scheme 2, 3a).²⁵ According to the general procedure, the reaction of benzoic (dibenzyl phosphoric) anhydride (0.2 mmol, 1.0 equiv), ethynylbenzene (0.6 mmol, 3.0 equiv), Pd(OAc)₂ (0.01 mmol, 5 mol %), XantPhos (0.02 mmol, 10 mol %) and Et₃N (0.3 mmol, 1.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography (hexane/dichloromethane = 10/1 to 1/1) the title compound in 81% yield (28.8 mg). White solid. ¹H NMR (400 MHz, CDCl₃) δ 7.55-7.53 (m, 4H), 7.36-7.34 (m, 6H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 131.7, 128.4, 128.3, 123.4, 89.4.

1,2-Diphenylethyne from benzoic (diphenyl phosphoric) anhydride and ethynylbenzene (Scheme 2, 3a).²⁵ According to the general procedure, the reaction of benzoic (diphenyl phosphoric) anhydride (0.2 mmol, 1.0 equiv), ethynylbenzene (0.6 mmol, 3.0 equiv), Pd(OAc)₂ (0.01 mmol, 5 mol %), XantPhos (0.02 mmol, 10 mol %) and Et₃N (0.3 mmol, 1.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography (hexane/dichloromethane = 10/1 to 1/1) the title compound in 71% yield (25.4 mg). White solid. ¹H NMR (400 MHz, CDCl₃) δ 7.55-7.53 (m, 4H), 7.36-7.34 (m, 6H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 131.7, 128.4, 128.3, 123.4, 89.4.

General Procedure for Competition Studies in Scheme 3. An oven-dried vial equipped with a stir bar was charged with carboxylic-phosphoric anhydride (1.0 equiv), alkyne A (2.0 equiv) and alkyne B (2.0 equiv), Pd(OAc)₂ (5 mol %), XantPhos (10 mol %), and Et₃N (1.5 equiv), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. Dioxane (0.20 M) was added with vigorous stirring at room temperature, and the reaction mixture was placed in a preheated oil bath at 160 °C and stirred for 15 h at 160 °C. Same operation as above, an oven-dried vial equipped with a stir bar was charged with carboxylic-phosphoric anhydride A (1.0 equiv), carboxylic-phosphoric anhydride B (1.0 equiv), and alkyne (0.5 equiv), Pd(OAc)₂ (5 mol %), XantPhos (10 mol %), and Et₃N (1.5 equiv), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. Dioxane (0.20 M) was added with vigorous stirring at room temperature, and the reaction mixture was placed in a preheated oil bath at 160 °C and stirred for 15 h at 160 °C. After the indicated time, the reaction mixture was cooled down to room temperature. After the indicated time, the reaction mixture was cooled down to room temperature, diluted with CH₂Cl₂ (10 mL), filtered, and concentrated. The sample was analyzed by GC–MS to obtain selectivity with authentic samples.

Data Availability Statement. The data underlying this study are available in the published article and its Supporting Information.

Supporting Information Available. ^1H NMR, ^{13}C NMR, ^{19}F NMR and ^{31}P NMR spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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