# Decarbonylative Alkynylation of Aryl Anhydrides via Palladium Catalysis

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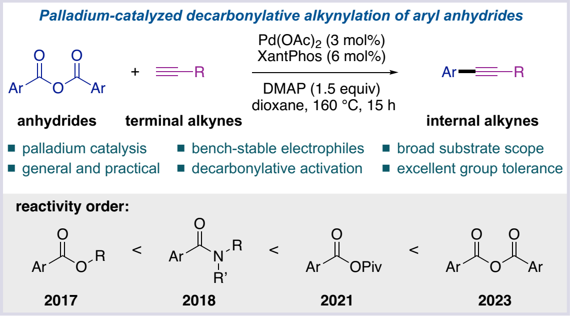
**TOC**



A robust palladium-catalyzed decarbonylative alkynylation of aryl anhydrides is reported. The catalytic system of $Pd(OAc)_2$/XantPhos and DMAP as a nucleophilic additive has been identified as effective promoters for decarbonylative Sonogashira alkynylation. Recently, activated esters, amides, and carboxylic acids were applied as electrophiles in transition-metal-catalyzed decarbonylative alkynylation. The present process expands this reactivity to readily available aryl anhydrides as electrophilic reagents for decarbonylative alkynylation. It is worth noting that the reactivity of aryl anhydrides is higher than that of esters, amides, and carboxylic acids in decarbonylative alkynylation. Broad substrate scope and excellent functional group tolerance is presented, demonstrating that aryl anhydrides may serve as general and practical class of electrophiles to achieve the synthesis of internal alkynes.

## Introduction

Alkynes are highly useful unsaturated hydrocarbons that contain at least one carbon-carbon triple bond.[1,2] Due to π-unsaturation and high chemical activity, alkynes are widely utilized as synthetic intermediates for a range of transformations, such as hydrogenation, hydration, oxidation, addition, and polymerization.[1] A small number of alkynes are present in nature, while most alkynes for synthetic use must be synthesized. The development of efficient protocols for the synthesis of alkynes is highly desirable. In this context, Sonogashira cross-coupling represents the most powerful, direct and widely used method for the synthesis of alkynes.[2] Traditional electrophiles for Sonogashira cross-coupling involve aryl halides and pseudohalides, which undergo direct oxidative addition of C–X bond and the formation of $C(sp^2)–C(sp)$ bond.[3] In particular, Sonogashira cross-coupling typically requires co-catalysis of palladium and copper, while systems based exclusively on palladium catalysis received less attention.[4]

In recent years, decarbonylative cross-coupling of carboxylic acid derivatives has entered the arena of organic synthesis.[5-7] Compared with typical aryl halides or pseudohalides, carboxylic acid derivatives used in decarbonylative reactions have several major advantages, such as broad availability, bench-stability, non-toxicity, and orthogonal reactivity to aryl halides and pseudohalides.[7] Therefore, decarbonylative alkynylation reactions involving carboxylic acid derivatives as electrophilic reagents has received much attention.[8] In 2017, Yamaguchi group reported a Pd/Cu-co-catalyzed decarbonylative Sonogashira cross-coupling of activated phenolic esters, permitting the synthesis of a series of aryl alkynes in 37-87% yields (Figure 1B).[9] Notably, in 2018, Chen and coworkers developed a Pd-catalyzed decarbonylative alkynylation of amides, a process which accomplished the conversion of amides to aryl alkynes without adding copper co-catalyst.[10] The synthesis of activated amides and esters requires converting carboxylic acids to acyl chlorides, and then reacting acyl chlorides with amines and phenols to obtain the corresponding activated amide and ester substrates.[11] To address this point, our group has developed decarbonylative cross-coupling reactions of carboxylic acids activated in situ, which can directly utilize carboxylic acids as substrates for various transformations.[7] The key point of this approach is the implementation of sterically hindered alkyl anhydrides, which can activate the aryl carboxylic acid substrates to aryl alkyl anhydrides. In 2021, Chen's research group[12] and our group[13] reported Pd-catalyzed decarbonylative alkynylation of carboxylic acids. However, this in situ activation process is often problematic by incompatibility of nucleophilic acylation and C–O oxidative addition steps.

Aryl anhydrides are cheap and readily available reagents that have been broadly utilized as substrates in synthetic organic chemistry.[14] We hypothesized that symmetrical aryl anhydrides can be employed in decarbonylative Sonogashira alkynylation with the advantages inherent to the stability and reactivity of aryl anhydrides in organic synthesis compared to other carboxylic acid derivatives. Herein, we report highly efficient palladium-catalyzed decarbonylative Sonogashira alkynylation of aryl anhydrides. Furthermore, we found that aryl anhydrides represent the most active electrophiles for decarbonylative alkynylation identified to date. Notable features of the study are as follows: (1) a robust method in the field of decarbonylative alkynylation of carboxylic acid derivatives; (2) excellent functional group tolerance and broad substrate scope; (3) the most active electrophiles for decarbonylative alkynylation.

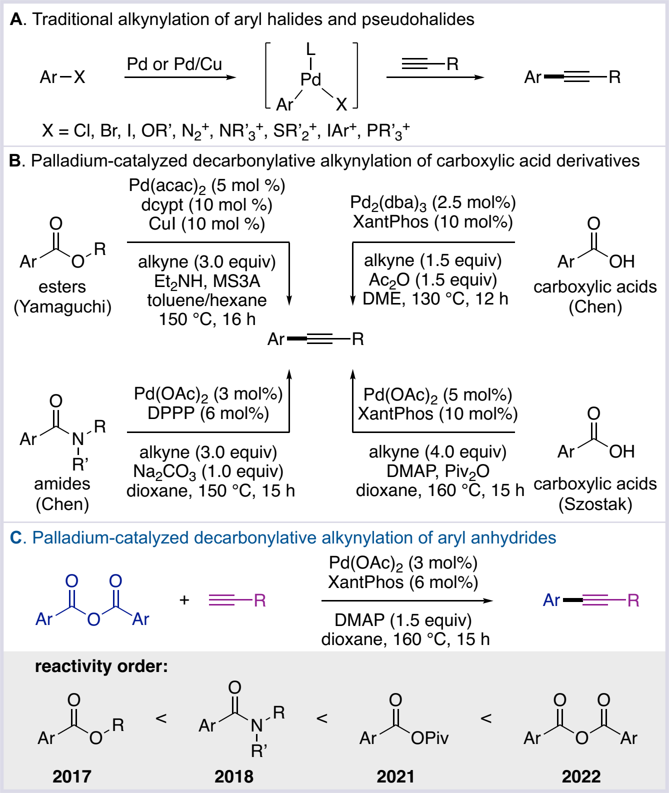


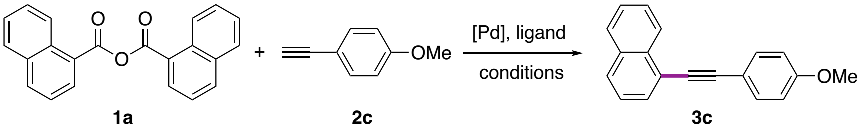
**Figure 1.** Development history of alkynylation reactions.

## Results and Discussion

The proposed decarbonylative alkynylation of aryl anhydrides was investigated using 1-naphthoic anhydride (**1a**) and 1-ethynyl-4-methoxybenzene (**2c**) as modular substrates. Optimization results are summarized in Table 1. The stoichiometry of alkynes was first screened (entries 1-3), and we found that 3 equivalents alkyne is the most economic ratio, affording excellent 96% yield (entry 1). Notably, various bases and base-free conditions were evaluated (entries 4-8), and we found that the reaction can be achieved under base-free conditions, affording 83% yield (entry 8). The yield could be further increased to 96% after adding DMAP as a nucleophilic additive (entry 1). A range of phosphine ligands were tested, and XantPhos was identified as the best ligand for this decarbonylative coupling (entries 9-17). A combination of steric hindrance, bite angle and electronic character of the phosphine ligand is critical for this decarbonylative transformation. A series of palladium catalysts have been screened, and the results shows that $Pd(OAc)_2$ is still the best catalyst for this reaction (entries 18-19). Toluene was tested as a potential solvent this reaction, affording modest yield of the cross-coupling product (entry

20). Interestingly, with the decrease of reaction temperature to 120 °C, the reaction still affords relatively high conversion, demonstrating the facile decarbonylation of this class of electrophiles (entries 21-22). The optimal reaction conditions involve 1-naphthoic anhydride **1a** (1.0 equiv), 1-ethynyl-4-methoxybenzene **2c** (3.0 equiv) in the presence of $Pd(OAc)_2$ (3 mol%) and XantPhos (6 mol%) in combination with DMAP (1.5 equiv) in dioxane at 160 °C, resulting in a close to quantitative conversion to the desired product **3c** (entry 1).

**Table 1. Summary of Optimization Studies**[a]



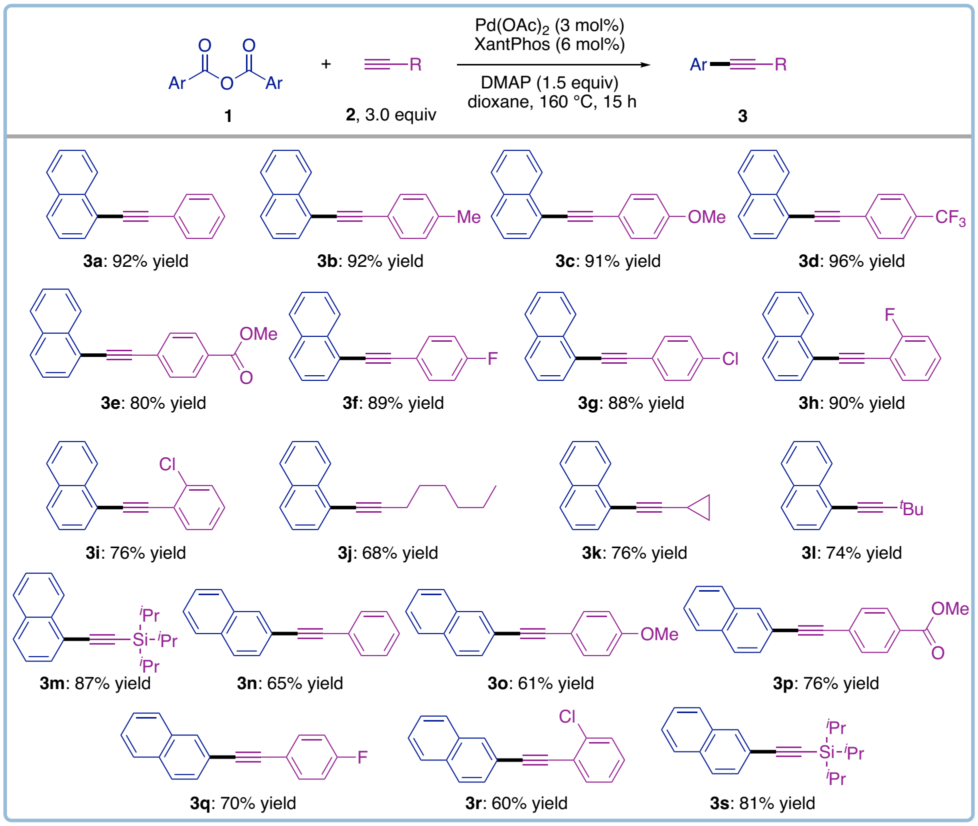
| entry | catalyst | ligand | base | yield[b](%) |
|---|---|---|---|---|
| 1 | $Pd(OAc)_2$ | XantPhos | DMAP | 96 |
| 2[c] | $Pd(OAc)_2$ | XantPhos | DMAP | 98 |
| 3[d] | $Pd(OAc)_2$ | XantPhos | DMAP | 86 |
| 4 | $Pd(OAc)_2$ | XantPhos | $Et_3N$ | 30 |
| 5 | $Pd(OAc)_2$ | XantPhos | Pyridine | 75 |
| 6 | $Pd(OAc)_2$ | XantPhos | $Na_2CO_3$ | 95 |
| 7 | $Pd(OAc)_2$ | XantPhos | $K_2CO_3$ | 64 |
| 8 | $Pd(OAc)_2$ | XantPhos | - | 83 |
| 9 | $Pd(OAc)_2$ | DPPP | DMAP | 68 |
| 10 | $Pd(OAc)_2$ | DPPB | DMAP | 52 |
| 11 | $Pd(OAc)_2$ | DPPPent | DMAP | 76 |
| 12 | $Pd(OAc)_2$ | BINAP | DMAP | 32 |
| 13 | $Pd(OAc)_2$ | XPhos | DMAP | 30 |
| 14 | $Pd(OAc)_2$ | SPhos | DMAP | 18 |
| 15 | $Pd(OAc)_2$ | $PCy_3HBF_4$ | DMAP | 20 |
| 16 | $Pd(OAc)_2$ | $PCyPh_2$ | DMAP | 11 |
| 17 | $Pd(OAc)_2$ | $PPh_3$ | DMAP | 31 |
| 18 | $PdCl_2$ | XantPhos | DMAP | 68 |
| 19 | $Pd_2(dba)_3$ | XantPhos | DMAP | 76 |
| 20[e] | $Pd(OAc)_2$ | XantPhos | DMAP | 53 |
| 21[f] | $Pd(OAc)_2$ | XantPhos | DMAP | 91 |
| 22[g] | $Pd(OAc)_2$ | XantPhos | DMAP | 86 |

[a]Standard conditions: 1-naphthoic anhydride **1a** (0.20 mmol, 1.0 equiv), 1-ethynyl-4-methoxybenzene **2c** (3.0 equiv), [Pd] (3 mol%), ligand (6 mol%), base (1.5 equiv), dioxane (0.20 M), 160 °C, 15 h; [b]Determined by $^1H$ NMR and/or GC. [c]1-ethynyl-4-methoxybenzene **2c** (4.0 equiv); [d]1-ethynyl-4-methoxybenzene **2c** (2.0 equiv); [e]toluene; [f]140 °C; [g]120 °C.

With the best conditions in hand, the substrate scope of this Pd-catalyzed decarbonylative Sonogashira alkynylation of aryl anhydrides was investigated (Scheme 1). The scope of terminal alkynes was first explored. Pleasingly, we found that various aryl alkynes bearing electron-neutral (**3a-**

**b**), electron-donating (**3c**), and electron-withdrawing (**3d**) substituents are well compatible with this process. Notably, alkyne substrate bearing ester group (**3e**) was well-tolerated under the standard conditions, showing compatibility with electrophilic carbonyl groups. Interestingly, substrates containing halogens, such as fluoro- (**3f**, **3h**) and chloro- (**3g**, **3i**), could also be well-converted into the desired alkynylation product by this approach. Furthermore, alkyl alkynes including primary (**3j**), secondary (**3k**) and tertiary (**3l-m**) alkynes could be readily employed in this method. Compared with 1-naphthoic acid, the carboxyl group of 2-naphthoic acid anhydride is more flexible and less sterically-hindered, while the alkynylation products are important intermediates in organic materials. Thus, the reactions of 2-naphthoic acid with various alkynes were tested. Pleasingly, we found that a range of terminal alkynes can be readily employed in this transformation, including electron-neutral (**3n**), electron-rich (**3o**) and electron-deficient aryl alkynes (**3p**). Furthermore, alkyne substrates containing fluoro (**3q**) and chloro (**3r**) groups are compatible under the standard conditions. Moreover, alkyl alkynes (**3s**) can also be well employed, delivering the desired alkynylation product in 81% yield.

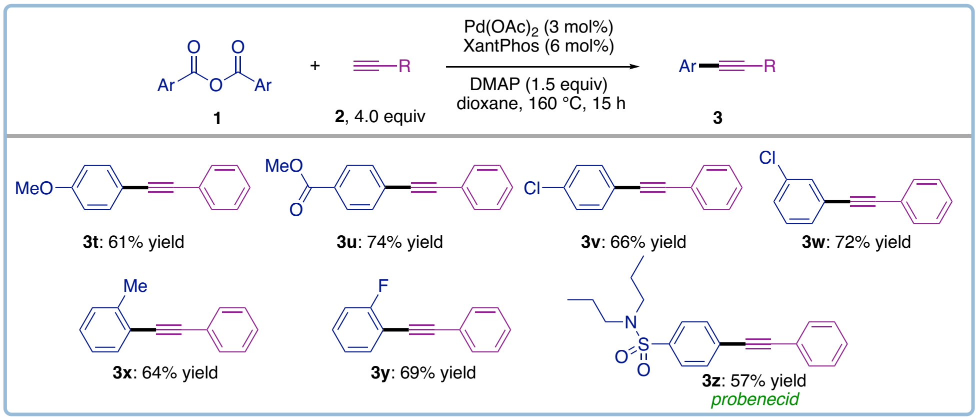
**Scheme 1.** Scope of Alkynes for Palladium-Catalyzed Decarbonylative Alkynylation of Aryl Anhydrides.[a]



[a]Conditions: naphthoic anhydride (0.1 mmol, 1.0 equiv), alkynes (3.0 equiv), $Pd(OAc)_2$ (3 mol %), XantPhos (6 mol %), DMAP (1.5 equiv), dioxane (0.2 M), 160 °C, 15 h.

Next, the substrate scope of aryl anhydrides has been explored (Scheme 2). Pleasingly, a series of benzoic anhydrides including electron-rich (**3t**) and electron-deficient (**3u**) substituents were well-tolerated by this method. Notably, substrates bearing halogens, such as chloro- (**3v-w**), fluoro- (**3y**), could be readily employed. Furthermore, sterically-hindered substrates, such as (**3x**), were also compatible, affording the desired alkynylation product in 64% yield. Finally, bioactive substrates are also compatible with this method, such as Probenecid, delivering the desired alkynylation product in good yield (**3z**). Overall, this method shows excellent functional group tolerance and broad substrate scope using robust and readily available aryl anhydrides as electrophiles for decarbonylative alkynylation.

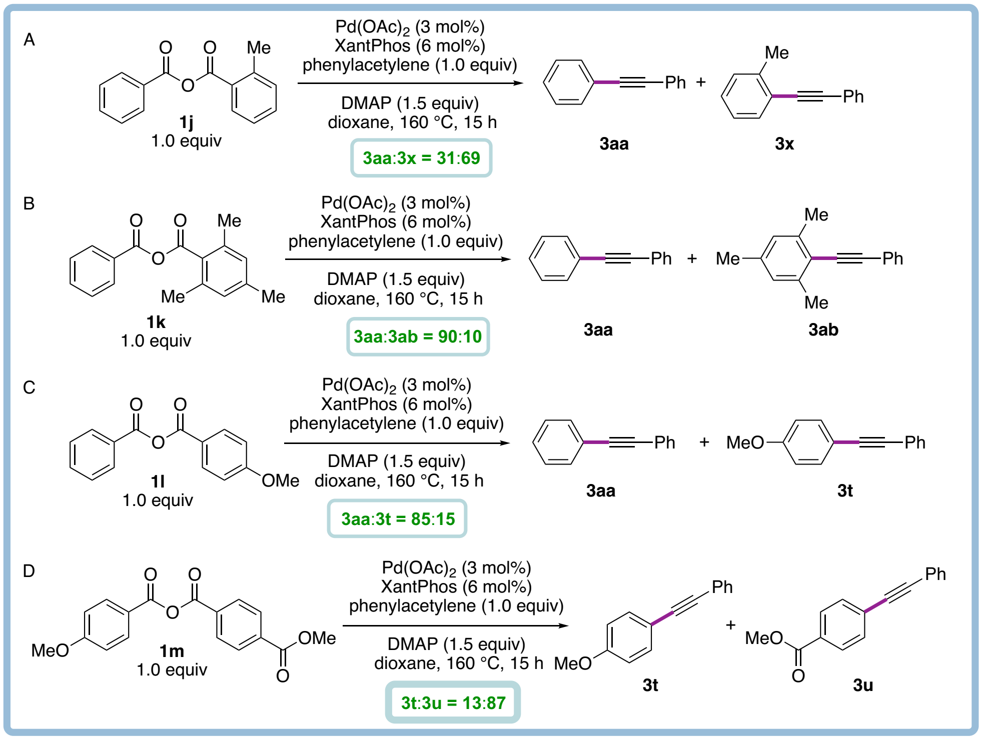
**Scheme 2.** Scope of Anhydrides for Palladium-Catalyzed Decarbonylative Alkynylation of Aryl Anhydrides.[a]



[a]Conditions: aryl anhydrides (0.1 mmol, 1.0 equiv), alkyne (3.0 equiv), $Pd(OAc)_2$ (3 mol %), XantPhos (6 mol %), DMAP (1.5 equiv), dioxane (0.2 M), 160 °C, 15 h.

A range of competition experiments were performed to gain insight into the selectivity of the present method (Scheme 3). As shown, aryl anhydride with one substituent at the ortho position undergoes coupling preferentially vs. the non-substituted substrate, indicating that appropriate steric hindrance in the substrate can promote the reaction (Scheme 3A). However, the reactivity of the anhydride substrate with substituents on both ortho positions is lower than that of non-substituted substrate, which is consistent with excessive steric hindrance inhibiting the reaction (Scheme 3B). Furthermore, the substrate with electron-neutral or electron-deficient group undergoes coupling preferentially vs. the substrate with electron-donating group (Scheme 3C-D), demonstrating that electron-rich groups can increase the activation energy for metal insertion into the C–O bond to facilitate the reaction.

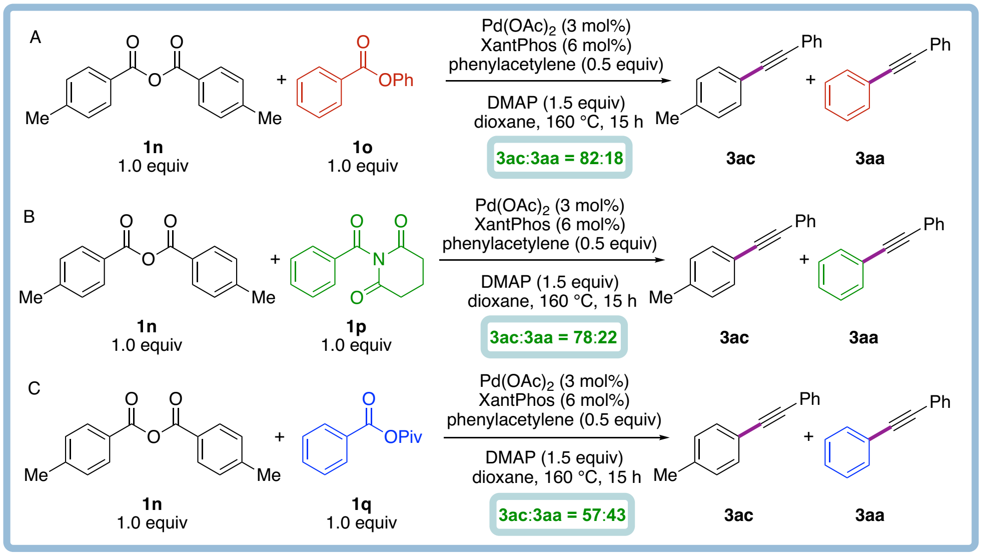
**Scheme 3.** Selectivity Studies in Palladium-Catalyzed Decarbonylative Alkynylation of Aryl Anhydrides.[a]



[a]Conditions: anhydrides (0.1 mmol, 1.0 equiv), phenylacetylene (1.0 equiv), $Pd(OAc)_2$ (3 mol %), XantPhos (6 mol %), DMAP (1.5 equiv), dioxane (0.2 M), 160 °C, 15 h.

Further competition experiments were conducted in order to gain insight into the reactivity difference vs. other carboxylic acid derivatives (Scheme 4). First, in order to understand the reactivity difference between anhydrides and esters in the decarbonylative alkynylation approach, competition experiment between anhydride vs. ester were performed (Scheme 4A). As expected, the reactivity of anhydride is significantly higher than that of ester. Furthermore, to gain insight into the reactivity difference between anhydrides and amides, competition experiments were performed (Scheme 4B). Importantly, anhydride electrophile in the present process is also more reactive than activated amide under the standard conditions. In addition, competition between symmetrical anhydride vs. unsymmetrical anhydride were performed (Scheme 4C). Interestingly, we found that the reactivity of symmetrical anhydride is higher than that of unsymmetrical anhydride.

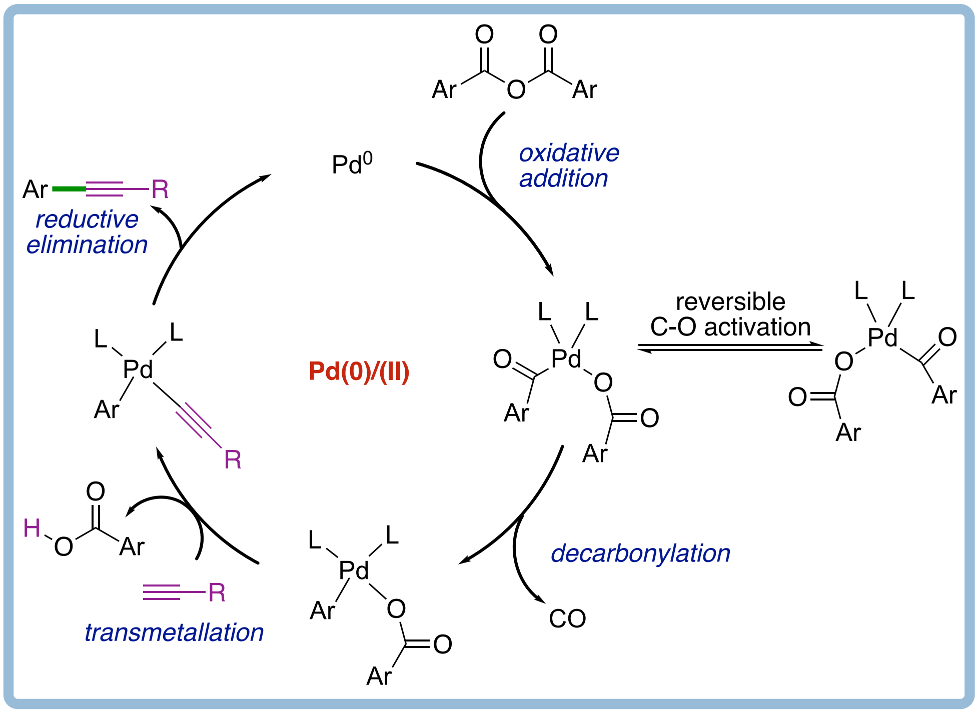
**Scheme 4.** Selectivity Studies in Palladium-Catalyzed Decarbonylative Alkynylation of Aryl Anhydrides.[a]



[a]Conditions: anhydrides (0.2 mmol, 1.0 equiv), other carboxylic acid derivatives (1.0 equiv), phenylacetylene (0.5 equiv), $Pd(OAc)_2$ (3 mol %), XantPhos (6 mol %), DMAP (1.5 equiv), dioxane (0.2 M), 160 °C, 15 h.

The proposed mechanism for this palladium-catalyzed decarbonylative alkynylation of aryl anhydrides is shown in Scheme 5. Firstly, palladium inserted into one of the (CO)–O bonds of aryl anhydrides, which involves a reversible C–O bond activation.[5-7] Oxidative addition is followed by decarbonylation. Next, alkyne replaces the carboxyl group by transmetallation, generating Ar–Pd–alkyne intermediate and carboxylate. Finally, desired alkynylation product and Pd catalysts are generated via reductive elimination. Carboxylic acid is considered to be a by-product of the reaction. Although aryl anhydrides have two aryl functional groups, only one aryl group can be converted into aryl alkynyl compounds, which is because the direct decarboxylative alkynylation of carboxylic acids generated in the decarbonylative process is difficult to occur under the current conditions. It should be noted that at present stage, alkyl anhydrides are incompatible due to β-hydride elimination.

**Scheme 5.** Proposed mechanism.



## Conclusions

In conclusion, the first palladium-catalyzed decarbonylative alkynylation of aryl anhydrides has been developed. The catalytic system of $Pd(OAc)_2$/XantPhos and DMAP as a nucleophilic additive has been identified as effective promoters for decarbonylative Sonogashira alkynylation. Broad substrate scope and excellent functional group tolerance has been achieved, demonstrating that aryl anhydrides may serve as general and practical class of electrophiles for the synthesis of internal alkynes. In the broader context, the discovery of decarbonylative alkynylation of readily available and bench-stable aryl anhydrides opens new prospects in the Sonogashira cross-coupling of carboxylic acid derivatives.

## 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. The Bruker 400 MHz spectrometer was used for NMR spectra generation.

**General Procedure for the Preparation of Aryl Anhydrides.** A previously published procedure was followed.[14c] An oven-dried flask (50 mL) equipped with a stir bar was charged with acyl chloride (5.0 mmol, 1.0 equiv) and pyridine (typically, 15 mL), placed under a positive pressure of argon. The reaction mixture was stirred 30 min at room temperature. After the indicated time, the reaction mixture was poured into ice water (50 mL). Then the mixture was filtrated and the filter cake was washed with ice water (10 mL) and hexane (10 mL). Unless stated otherwise, the crude product was purified by recrystallization (ethyl acetate/hexane) to give analytically pure product.

**General Procedure for the Preparation of Asymmetric Anhydrides.** A previously published procedure was followed.[15] An oven-dried flask (50 mL) equipped with a stir bar was charged with benzoic acid (typically, 5.0 mmol, 1.0 equiv), triethylamine (typically, 10.0 mmol, 2.0 equiv) and tetrahydrofuran (typically, 0.50 M), placed under a positive pressure of argon. Acyl chloride (typically, 1.0 equiv) was added portions to the reaction mixture with vigorous stirring at room temperature, and the reaction mixture was stirred for 30 min. After the indicated time, the reaction mixture was diluted with ethyl acetate (30 mL). The reaction mixture was washed with HCl (10 mL), $H_2O$ (10 mL), brine (10 mL), dried, and concentrated to get crude product. Unless stated otherwise, the crude product was purified by recrystallization (ethyl acetate/hexane) to give analytically pure product.

**General Procedure for Palladium-Catalyzed Alkynylation of Aryl Anhydrides.** An oven-dried vial equipped with a stir bar was charged with aryl anhydride (neat, 1.0 equiv), alkyne (neat, 3.0 equiv), $Pd(OAc)_2$ (typically, 3 mol%), XantPhos (typically, 6 mol%), and DMAP (neat, 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, 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 (hexane/dichloromethane) afforded the title products. 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 Alkynylation of Aryl Anhydrides.** An oven-dried vial equipped with a stir bar was charged with 2-naphthoic anhydride (neat, 65.3 mg, 0.20 mmol), 1-ethynyl-4-methoxybenzene (79.3 mg, 0.6 mmol, 3.0 equiv), $Pd(OAc)_2$ (1.4 mg, 0.006 mmol, 3 mol%), XantPhos (6.9 mg, 0.012 mmol, 6 mol%), and DMAP (neat, 36.7 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, 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 91% (46.5 mg, 0.18 mmol). White solid. Characterization data are included in the section below.

**Large Scale Example for Palladium-Catalyzed Alkynylation of Aryl Anhydrides**. An oven-dried vial equipped with a stir bar was charged with 1-naphthoic anhydride (neat, 326.4 mg, 1.0 mmol), ethynylbenzene (306.4 mg, 3.0 mmol, 3.0 equiv), $Pd(OAc)_2$ (6.8 mg, 0.03 mmol, 3 mol%), XantPhos (34.8 mg, 0.06 mmol, 6 mol%), and DMAP (neat, 183.3 mg, 1.5 mmol, 1.5 equiv), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. Dioxane (5.0 mL, 0.20 M) was added with vigorous stirring at room temperature, 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 (hexane/dichloromethane = 10/1 to 1/1) afforded the title product. Isolated yield 80% (182.4 mg, 0.8 mmol). White solid. Characterization data are included in the section below.

**1-Naphthoic anhydride (1a).**[14c] Yield: 94% (1.53 g). White solid. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.88-7.86 (d, *J* = 8.0 Hz, 2 H), 7.66-7.62 (t, *J* = 8.0 Hz, 1 H), 7.51-7.47 (t, *J* = 8.0 Hz, 2 H), 2.80-2.76 (t, *J* =

8.0 Hz, 4 H), 2.19-2.12 (m, 2 H). **$^{13}$C{$^{1}$H} NMR (100 MHz, CDCl$_3$)** δ 163.1, 135.7, 134.1, 132.3, 132.0, 128.9, 126.9, 125.8, 125.0, 124.6.

**2-Naphthoic anhydride (1b)**.[14c] Yield: 92% (1.51 g). White solid. **$^{1}$H NMR (400 MHz, CDCl$_3$)** δ 8.78 (s, 2 H), 8.19 (dd, $J^1$ = 8.6 Hz, $J^2$ = 1.8 Hz, 2 H), 8.03-7.93 (m, 6 H), 7.69-7.65 (m, 2 H), 7.62-7.58 (m, 2 H). **$^{13}$C{$^{1}$H} NMR (100 MHz, CDCl$_3$)** δ 162.9, 136.3, 132.9, 132.5, 129.8, 129.4, 129.0, 128.0, 127.3, 126.2, 125.5

**4-Methoxybenzoic anhydride (1c)**.[14c] Yield: 80% (1.15 g). White solid. **$^{1}$H NMR (400 MHz, CDCl$_3$)** δ 8.09 (d, $J$ = 8.9 Hz, 4 H), 6.97 (d, $J$ = 8.8 Hz, 4 H), 3.88 (s, 6 H). **$^{13}$C{$^{1}$H} NMR (100 MHz, CDCl$_3$)** δ 164.7, 162.4, 132.9, 121.3, 114.2, 55.7.

**4-(Methoxycarbonyl)benzoic anhydride (1d).**[14c] Yield: 71% (1.22 g). White solid. **$^{1}$H NMR (400 MHz, CDCl$_3$)** δ 8.23-8.17 (m, 8 H), 3.97 (s, 6 H). **$^{13}$C{$^{1}$H} NMR (100 MHz, CDCl$_3$)** δ 166.0, 161.4, 135.6, 132.3, 130.6, 130.2, 52.8.

**4-Chlorobenzoic anhydride (1e).**[14c] Yield: 83% (1.22 g). White solid. **$^{1}$H NMR (400 MHz, CDCl$_3$)** δ 8.08 (d, $J$ = 8.6 Hz, 4 H), 7.51 (d, $J$ = 8.6 Hz, 4 H). **$^{13}$C{$^{1}$H} NMR (100 MHz, CDCl$_3$)** δ 161.4, 141.6, 132.0, 129.5, 127.2.

**3-Chlorobenzoic anhydride (1f).**[14c] Yield: 87% (1.28 g). White solid. **$^{1}$H NMR (400 MHz, CDCl$_3$)** δ 8.10 (s, 2 H), 8.03 (d, $J$ = 7.7 Hz, 2 H), 7.66 (dd, $J^1$ = 8.0 Hz, $J^2$ = 1.1 Hz, 2 H), 7.49 (t, $J$ = 7.9 Hz, 2 H). **$^{13}$C{$^{1}$H} NMR (100 MHz, CDCl$_3$)** δ 161.0, 135.3, 134.9, 130.6, 130.4, 130.3, 128.8.

**2-Methylbenzoic anhydride (1g).**[14c] Yield: 72% (0.92 g). White solid. **$^{1}$H NMR (400 MHz, CDCl$_3$)** δ 8.06 (d, $J$ = 8.0 Hz, 2 H), 7.51 (td, $J^1$ = 7.5 Hz, $J^2$ = 1.5 Hz, 2 H), 7.35-7.30 (m, 4 H), 2.71 (s, 6 H). **$^{13}$C{$^{1}$H} NMR (100 MHz, CDCl$_3$)** δ 163.0, 142.7, 133.7, 132.4, 131.5, 127.8, 126.2, 22.1.

**2-Fluorobenzoic anhydride (1h).**[14c] Yield: 83% (1.09 g). Brown solid. **$^{1}$H NMR (400 MHz, CDCl$_3$)** δ 8.10-8.05 (m, 2 H), 7.67-7.61 (m, 2 H), 7.31-7.27 (m, 2 H), 7.24-7.18 (m, 2 H). **$^{13}$C{$^{1}$H} NMR (100**

**MHz, CDCl$_3$)** δ 162.7 (d, $J$ = 261.4 Hz), 159.5 (d, $J$ = 2.5 Hz), 136.5 (d, $J$ = 9.9 Hz), 133.0, 124.6 (d, $J$ = 3.8 Hz), 117.5 (d, $J$ = 22.3 Hz), 117.2 (d, $J$ = 8.4 Hz). **$^{19}$F NMR (376 MHz, CDCl$_3$)** δ -107.65.

**4-(*N*,*N*-Dipropylsulfamoyl)benzoic anhydride (1i)**.[14c] Yield: 68% (1.88 g). White solid. **$^{1}$H NMR (400 MHz, CDCl$_3$)** δ 8.28-8.25 (m, 4 H), 7.98-7.96 (m, 4 H), 3.14-3.11 (m, 8 H), 1.61-1.51 (m, 8 H), 0.87 (t, $J$ = 7.4 Hz, 12 H). **$^{13}$C{$^{1}$H} NMR (100 MHz, CDCl$_3$)** δ 160.8, 146.2, 131.6, 131.3, 127.6, 50.0, 22.0, 11.3.

**Benzoic 2-methylbenzoic anhydride (1j).**[14c] Yield: 85% (1.02 g). White solid. **$^{1}$H NMR (500 MHz, CDCl$_3$)** δ 8.18-8.17 (d, $J$ = 7.3 Hz, 2 H), 8.09-8.07 (d, $J$ = 7.9 Hz, 1 H), 7.71-7.68 (t, $J$ = 7.5 Hz, 1 H), 7.57-7.52 (m, 3 H), 7.37-7.34 (t, $J$ = 7.4 Hz, 2 H). **$^{113}$C{$^{1}$H} NMR (125 MHz, CDCl$_3$)** δ 162.8, 162.5, 142.7, 134.4, 133.7, 132.3, 131.5, 130.5, 129.1, 128.9, 127.7, 126.1, 22.0.

**Benzoic 2,4,6-trimethylbenzoic anhydride (1k).**[14c] Yield: 90% (1.21 g). White solid. **$^{1}$H NMR (500 MHz, CDCl$_3$)** δ 8.20-8.18 (d, $J$ = 7.2 Hz, 1 H), 8.14-8.13 (d, $J$ = 7.2 Hz, 1 H), 7.66-7.63 (t, $J$ = 7.4 Hz, 1 H), 7.57-7.54 (t, $J$ = 8.0 Hz, 1 H), 7.52-7.49 (t, $J$ = 7.7 Hz, 1 H), 6.91 (s, 2 H), 2.42 (s, 6 H), 2.32 (s, 3 H). **$^{13}$C{$^{1}$H} NMR (125 MHz, CDCl$_3$)** δ 175.0, 171.8, 140.1, 136.1, 133.8, 130.6, 130.2, 128.9, 128.8, 128.5, 21.2, 20.3.

**Benzoic 4-methoxybenzoic anhydride (1l).**[14c] Yield: 72% (0.92 g). White solid. **$^{1}$H NMR (500 MHz, CDCl$_3$)** δ 8.18-8.17 (d, $J$ = 7.2 Hz, 2 H), 8.14-8.12 (d, $J$ = 9.0 Hz, 2 H), 7.70-7.67 (t, $J$ = 7.4 Hz, 1 H), 7.56-7.53 (t, $J$ = 8.1 Hz, 2 H), 7.02-7.00 (d, $J$ = 9.0 Hz, 2 H), 3.92 (s, 3 H). **$^{13}$C{$^{1}$H} NMR (125 MHz, CDCl$_3$)** δ 164.7, 162.6, 162.1, 134.4, 132.9, 130.5, 129.1, 128.8, 121.1, 114.2, 55.6.

**4-Methoxybenzoic 4-(methoxycarbonyl)benzoic anhydride (1m)**. Yield: 86% (1.35 g). *New Compound*. White solid. **$^{1}$H NMR (400 MHz, CDCl$_3$)** δ 8.23-8.16 (m, 4 H), 8.12-8.09 (d, $J$ = 9.0 Hz, 2 H), 7.02-6.97 (m, 2 H), 3.97 (s, 3 H), 3.91 (s, 3 H). **$^{13}$C{$^{1}$H} NMR (100 MHz, CDCl$_3$)** δ 165.0, 162.0, 161.8, 135.2, 133.2, 133.0, 130.5, 130.1, 120.8, 114.4, 114.3, 55.8, 52.8. **HRMS (ESI)** m/z calcd for $C_{17}H_{15}O_6$ $(M+H)^+$ 315.0863, found 315.0867.

**4-Methylbenzoic anhydride (1n).**[14c] Yield: 80% (1.02 g). White solid. **<u>$^1$H NMR (400 MHz, $CDCl_3$)</u>** δ 8.04 (d, *J* = 8.3 Hz, 2 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 2.45 (s, 3 H). **<u>$^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$)</u>** δ 162.7, 145.7, 130.8, 129.7, 126.3, 22.0.

**Phenyl benzoate (1o)**.[16] Yield: 90% (0.93 g). White solid. **<u>$^1$H NMR (400 MHz, $CDCl_3$)</u>** δ 8.22-8.20 (m, 2 H), 7.65-7.61 (t, *J* = 7.4 Hz, 1 H), 7.52-7.48 (t, *J* = 7.8 Hz, 2 H), 7.45-7.40 (m, 2 H), 7.29-7.25 (t, *J* = 7.4 Hz, 1 H), 7.23-7.20 (m, 2 H). **<u>$^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$)</u>** δ 165.3, 151.0, 133.7, 130.3, 129.7, 129.6, 128.7, 126.0, 121.8.

**1-Benzoylpiperidine-2,6-dione (1p).**[14c] Yield: 80% (0.867 g). White solid. **<u>$^1$H NMR (400 MHz, $CDCl_3$)</u>** δ 7.88-7.86 (d, *J* = 8.0 Hz, 2 H), 7.66-7.62 (t, *J* = 8.0 Hz, 1 H), 7.51-7.47 (t, *J* = 8.0 Hz, 2 H), 2.80-2.76 (t, *J* = 8.0 Hz, 4 H), 2.19-2.12 (m, 2 H). **<u>$^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$)</u>** δ 172.0, 170.9, 135.1, 131.9, 130.3, 129.3, 32.5, 17.6.

**Benzoic pivalic anhydride (1q).**[14c] Yield: 91% (0.94 g). Colorless oil. **<u>$^1$H NMR (400 MHz, $CDCl_3$)</u>** δ 8.02 (d, *J* = 8.3 Hz, 2 H), 7.63-7.59 (m, 1 H), 7.46 (t, *J* = 7.8 Hz, 2 H), 1.35 (s, 9 H). **<u>$^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$)</u>** δ 173.7, 162.5, 134.4, 130.3, 128.8, 40.3, 26.5.

**1-(Phenylethynyl)naphthalene (Scheme 1, 3a).**[13] According to the general procedure, the reaction of 1-naphthoic anhydride (0.2 mmol), ethynylbenzene (0.6 mmol, 3.0 equiv), $Pd(OAc)_2$ (0.006 mmol, 3 mol%), XantPhos (0.012 mmol, 6 mol%), and DMAP (0.3 mmol, 1.5 equiv) in dioxane (0.20 M) for 15 h at 160 °C, after work-up and chromatography (hexane/dichloromethane = 10/1 to 1/1) afforded the title compound in 92% yield (41.9 mg). White solid. **<u>$^1$H NMR (400 MHz, $CDCl_3$)</u>** δ 8.47 (d, *J* = 8.3 Hz, 1 H), 7.87 (t, *J* = 9.1 Hz, 2 H), 7.79 (dd, $J^1$ = 7.2 Hz, $J^2$ = 1.2 Hz, 1 H), 7.69-7.66 (m, 2 H), 7.64-7.60 (m, 1 H), 7.57-7.53 (m, 1 H), 7.50-7.46 (m, 1 H), 7.44-7.37 (m, 3 H). **<u>$^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$)</u>** δ 133.4, 133.3, 131.8, 130.5, 128.9, 128.6, 128.5, 128.4, 126.9, 126.6, 126.4, 125.4, 123.5, 121.0, 94.4, 87.6.

**1-(*p*-Tolylethynyl)naphthalene (Scheme 1, 3b).**[12] According to the general procedure, the reaction of 1-naphthoic anhydride (0.2 mmol), 1-ethynyl-4-methylbenzene (0.6 mmol, 3.0 equiv), Pd(OAc)$_2$ (0.006 mmol, 3 mol%), XantPhos (0.012 mmol, 6 mol%), and DMAP (0.3 mmol, 1.5 equiv) in dioxane (0.20 M) for 15 h at 160 °C, after work-up and chromatography (hexane/dichloromethane = 10/1 to 1/1) afforded the title compound in 92% yield (44.5 mg). White solid. **$^1$H NMR (400 MHz, CDCl$_3$)** δ 8.47 (d, $J$ = 8.3 Hz, 1 H), 7.86 (dd, $J^1$ = 13.0 Hz, $J^2$ = 8.2 Hz, 2 H), 7.78 (dd, $J^1$ = 7.2 Hz, $J^2$ = 1.2 Hz, 1 H), 7.64-7.60 (m, 1 H), 7.58-7.53 (m, 3 H), 7.49-7.45 (m, 1 H), 7.23 (d, $J$ = 7.8 Hz, 2 H), 2.42 (s, 3 H). **$^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$)** δ 138.7, 133.4, 133.3, 131.7, 130.3, 129.3, 128.7, 128.4, 126.8, 126.5, 126.4, 125.4, 121.2, 120.4, 94.7, 87.0, 21.7.

**1-((4-Methoxyphenyl)ethynyl)naphthalene (Scheme 1, 3c).**[13] According to the general procedure, the reaction of 1-naphthoic anhydride (0.2 mmol), 1-ethynyl-4-methoxybenzene (0.6 mmol, 3.0 equiv), Pd(OAc)$_2$ (0.006 mmol, 3 mol%), XantPhos (0.012 mmol, 6 mol%), and DMAP (0.3 mmol, 1.5 equiv) in dioxane (0.20 M) for 15 h at 160 °C, after work-up and chromatography (hexane/dichloromethane = 10/1 to 1/1) afforded the title compound in 91% yield (46.9 mg). Light yellow solid. **$^1$H NMR (400 MHz, CDCl$_3$)** δ 8.46 (d, $J$ = 8.3 Hz, 1 H), 7.85 (dd, $J^1$ = 15.6 Hz, $J^2$ = 8.2 Hz, 2 H), 7.75 (dd, $J^1$ = 7.1 Hz, $J^2$ = 1.2 Hz, 1 H), 7.62-7.59 (m, 3 H), 7.56-7.52 (m, 1 H), 7.46 (dd, $J^1$ = 8.3 Hz, $J^2$ = 7.1 Hz, 1 H), 6.94 (d, $J$ = 8.8 Hz, 2 H), 3.86 (s, 3 H). **$^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$)** δ 159.9, 133.4, 133.3, 130.2, 128.5, 128.4, 126.8, 126.5, 126.4, 125.4, 121.4, 115.6, 114.2, 94.5, 86.3, 55.5.

**1-((4-(Trifluoromethyl)phenyl)ethynyl)naphthalene (Scheme 1, 3d).**[12] According to the general procedure, the reaction of 1-naphthoic anhydride (0.2 mmol), 1-ethynyl-4-(trifluoromethyl)benzene (0.6 mmol, 3.0 equiv), Pd(OAc)$_2$ (0.006 mmol, 3 mol%), XantPhos (0.012 mmol, 6 mol%), and DMAP (0.3 mmol, 1.5 equiv) in dioxane (0.20 M) for 15 h at 160 °C, after work-up and chromatography (hexane/dichloromethane = 10/1 to 1/1) afforded the title compound in 96% yield (56.8 mg). White solid. **$^1$H NMR (400 MHz, CDCl$_3$)** δ 8.42 (d, $J$ = 8.3 Hz, 1 H), 7.89 (d, $J$ = 8.1 Hz, 2 H), 7.80 (dd, $J^1$ = 7.1 Hz, $J^2$ = 1.2 Hz, 1 H), 7.75 (d, $J$ = 8.1 Hz, 2 H), 7.66 (d, $J$ = 8.3 Hz, 2 H), 7.63-7.61 (m, 1 H), 7.58-

7.54 (m, 1 H), 7.49 (dd, $J^1$ = 8.3 Hz, $J^2$ = 7.2 Hz, 1 H). **$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)** δ 133.3, 132.0, 130.9, 130.1 (q, $J^F$ = 32.5 Hz), 129.5, 128.6, 127.3, 127.1, 126.7, 126.1, 125.5 (q, $J^F$ = 3.7 Hz), 125.4, 122.7, 120.3, 92.9, 90.1. **$^{19}F$ NMR (376 MHz, $CDCl_3$)** δ -62.72.

**Methyl 4-(naphthalen-1-ylethynyl)benzoate (Scheme 1, 3e).**[17] According to the general procedure, the reaction of 1-naphthoic anhydride (0.2 mmol), methyl 4-ethynylbenzoate (0.6 mmol, 3.0 equiv), $Pd(OAc)_2$ (0.006 mmol, 3 mol%), XantPhos (0.012 mmol, 6 mol%), and DMAP (0.3 mmol, 1.5 equiv) in dioxane (0.20 M) for 15 h at 160 °C, after work-up and chromatography (hexane/dichloromethane = 10/1 to 1/1) afforded the title compound in 80% yield (45.8 mg). Light yellow solid. **$^1H$ NMR (400 MHz, $CDCl_3$)** δ 8.42 (d, $J$ = 8.3 Hz, 1 H), 8.07 (d, $J$ = 8.5 Hz, 2 H), 7.88 (d, $J$ = 7.9 Hz, 2 H), 7.79 (dd, $J^1$ = 7.2 Hz, $J^2$ = 1.2 Hz, 1 H), 7.71 (d, $J$ = 8.4 Hz, 2 H), 7.64-7.60 (m, 1 H), 7.57-7.53 (m, 1 H), 7.48 (dd, $J^1$ = 8.3 Hz, $J^2$ = 7.1 Hz, 1 H), 3.95 (s, 3 H). **$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)** δ 166.7, 133.3, 131.7, 130.9, 129.74, 129.68, 129.5, 128.5, 128.2, 127.1, 126.7, 126.2, 125.4, 120.4, 93.6, 90.7, 52.4.

**1-((4-Fluorophenyl)ethynyl)naphthalene (Scheme 1, 3f).**[12] According to the general procedure, the reaction of 1-naphthoic anhydride (0.2 mmol), 1-ethynyl-4-fluorobenzene (0.6 mmol, 3.0 equiv), $Pd(OAc)_2$ (0.006 mmol, 3 mol%), XantPhos (0.012 mmol, 6 mol%), and DMAP (0.3 mmol, 1.5 equiv) in dioxane (0.20 M) for 15 h at 160 °C, after work-up and chromatography (hexane/dichloromethane = 10/1 to 1/1) afforded the title compound in 89% yield (43.7 mg). White solid. **$^1H$ NMR (400 MHz, $CDCl_3$)** δ 8.42 (d, $J$ = 8.3 Hz, 1 H), 7.87 (t, $J$ = 8.6 Hz, 2 H), 7.76 (dd, $J^1$ = 7.2 Hz, $J^2$ = 1.2 Hz, 1 H), 7.66-7.59 (m, 3 H), 7.57-7.53 (m, 1 H), 7.47 (dd, $J^1$ = 8.3 Hz, $J^2$ = 7.1 Hz, 1 H), 7.13-7.07 (m, 2 H). **$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)** δ 162.7 (d, $J^F$ = 248.0 Hz), 133.7 (d, $J^F$ = 8.2 Hz), 133.3, 130.5, 129.0, 128.5, 126.9, 126.6, 126.3, 125.4, 120.8, 119.6 (d, $J^F$ = 3.4 Hz), 116.0, 115.8, 93.3, 87.3. **$^{19}F$ NMR (376 MHz, $CDCl_3$)** δ -110.74.

**1-((4-Chlorophenyl)ethynyl)naphthalene (Scheme 1, 3g).**[12] According to the general procedure, the reaction of 1-naphthoic anhydride (0.2 mmol), 1-chloro-4-ethynylbenzene (0.6 mmol, 3.0 equiv),

$Pd(OAc)_2$ (0.006 mmol, 3 mol%), XantPhos (0.012 mmol, 6 mol%), and DMAP (0.3 mmol, 1.5 equiv) in dioxane (0.20 M) for 15 h at 160 °C, after work-up and chromatography (hexane/dichloromethane = 10/1 to 1/1) afforded the title compound in 88% yield (46.1 mg). White solid. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.40 (d, *J* = 8.3 Hz, 1 H), 7.87 (t, *J* = 7.4 Hz, 3 H), 7.76 (dd, $J^1$ = 7.2 Hz, $J^2$ = 1.3 Hz, 1 H), 7.63-7.53 (m, 4 H), 7.47 (dd, $J^1$ = 8.3 Hz, $J^2$ = 7.1 Hz, 1 H), 7.38 (d, *J* = 8.5 Hz, 2 H). **$^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$)** δ 134.5, 133.33, 133.31, 133.0, 130.6, 129.2, 128.9, 128.5, 127.0, 126.6, 126.2, 125.4, 122.0, 120.7, 93.3, 88.6.

**1-((2-Fluorophenyl)ethynyl)naphthalene (Scheme 1, 3h).**[12] According to the general procedure, the reaction of 1-naphthoic anhydride (0.2 mmol), 1-ethynyl-2-fluorobenzene (0.6 mmol, 3.0 equiv), $Pd(OAc)_2$ (0.006 mmol, 3 mol%), XantPhos (0.012 mmol, 6 mol%), and DMAP (0.3 mmol, 1.5 equiv) in dioxane (0.20 M) for 15 h at 160 °C, after work-up and chromatography (hexane/dichloromethane = 10/1 to 1/1) afforded the title compound in 90% yield (44.3 mg). Yellow solid. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.49 (d, *J* = 8.3 Hz, 1 H), 7.88 (dd, $J^1$ = 8.3 Hz, $J^2$ = 3.6 Hz, 2 H), 7.80 (d, *J* = 7.2 Hz, 1 H), 7.66-7.61 (m, 2 H), 7.55 (t, *J* = 7.4 Hz, 1 H), 7.48 (t, *J* = 7.7 Hz, 1 H), 7.39-7.33 (m, 1 H), 7.20-7.15 (m, 2 H). **$^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$)** δ 162.9 (d, $J^F$ = 251.7 Hz), 133.5, 133.4, 133.3, 130.6, 130.2 (d, $J^F$ = 7.8 Hz), 129.3, 128.4, 127.1, 126.6, 126.4, 125.4, 124.2 (d, $J^F$ = 3.8 Hz), 120.7, 115.7 (d, $J^F$ = 20.8 Hz), 112.2 (d, $J^F$ = 15.7 Hz), 92.8 (d, $J^F$ = 3.3 Hz), 87.7. **$^{19}$F NMR (376 MHz, $CDCl_3$)** δ -109.47.

**1-((2-Chlorophenyl)ethynyl)naphthalene (Scheme 1, 3i).**[18] According to the general procedure, the reaction of 1-naphthoic anhydride (0.2 mmol), 1-chloro-2-ethynylbenzene (0.6 mmol, 3.0 equiv), $Pd(OAc)_2$ (0.006 mmol, 3 mol%), XantPhos (0.012 mmol, 6 mol%), and DMAP (0.3 mmol, 1.5 equiv) in dioxane (0.20 M) for 15 h at 160 °C, after work-up and chromatography (hexane/dichloromethane = 10/1 to 1/1) afforded the title compound in 76% yield (39.8 mg). Yellow solid. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.57 (d, *J* = 8.3 Hz, 1 H), 7.88 (d, *J* = 8.1 Hz, 2 H), 7.82 (dd, $J^1$ = 7.1 Hz, $J^2$ = 1.2 Hz, 1 H), 7.70-7.67 (m, 1 H), 7.64-7.60 (m, 1 H), 7.57-7.53 (m, 1 H), 7.50-7.46 (m, 2 H), 7.31-7.29 (m, 2 H).

**$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)** δ 136.0, 133.5, 133.4, 133.3, 130.8, 129.52, 129.47, 129.3, 128.4, 127.1, 126.69, 126.65, 126.5, 125.4, 123.5, 120.7, 92.9, 91.1.

**1-(Oct-1-yn-1-yl)naphthalene (Scheme 1, 3j)**.[19] According to the general procedure, the reaction of 1-naphthoic anhydride (0.2 mmol), oct-1-yne (0.6 mmol, 3.0 equiv), $Pd(OAc)_2$ (0.006 mmol, 3 mol%), XantPhos (0.012 mmol, 6 mol%), and DMAP (0.3 mmol, 1.5 equiv) in dioxane (0.20 M) for 15 h at 160 °C, after work-up and chromatography (hexane/dichloromethane = 10/1 to 1/1) afforded the title compound in 68% yield (32.1 mg). Yellow oil. **$^1H$ NMR (400 MHz, $CDCl_3$)** δ 8.36 (d, $J$ = 8.3 Hz, 1 H), 7.84 (d, $J$ = 7.6 Hz, 1 H), 7.78 (d, $J$ = 8.3 Hz, 1 H), 7.64 (dd, $J^1$ = 7.1 Hz, $J^2$ = 1.2 Hz, 1 H), 7.59-7.54 (m, 1 H), 7.53-7.49 (m, 1 H), 7.41 (dd, $J^1$ = 8.3 Hz, $J^2$ = 7.1 Hz, 1 H). **$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)** δ 133.6, 133.3, 130.1, 128.3, 128.0, 126.6, 126.5, 126.3, 125.4, 121.9, 95.7, 78.7, 31.5, 29.0, 28.9, 22.8, 19.9, 14.2.

**1-(Cyclopropylethynyl)naphthalene (Scheme 1, 3k).**[12] According to the general procedure, the reaction of 1-naphthoic anhydride (0.2 mmol), ethynylcyclopropane (0.6 mmol, 3.0 equiv), $Pd(OAc)_2$ (0.006 mmol, 3 mol%), XantPhos (0.012 mmol, 6 mol%), and DMAP (0.3 mmol, 1.5 equiv) in dioxane (0.20 M) for 15 h at 160 °C, after work-up and chromatography (hexane/dichloromethane = 10/1 to 1/1) afforded the title compound in 76% yield (29.2 mg). Light yellow solid. **$^1H$ NMR (400 MHz, $CDCl_3$)** δ 8.31 (d, $J$ = 8.3 Hz, 1 H), 7.83 (d, $J$ = 7.9 Hz, 1 H), 7.77 (d, $J$ = 8.3 Hz, 1 H), 7.61 (dd, $J^1$ = 7.2 Hz, $J^2$ = 1.2 Hz, 1 H), 7.57-7.53 (m, 1 H), 7.52-7.48 (m, 1 H), 7.39 (dd, $J^1$ = 8.3 Hz, $J^2$ = 7.1 Hz, 1 H), 1.65-1.58 (m, 1 H), 0.99-0.91 (m, 4 H). **$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)** δ 133.7, 133.3, 130.2, 128.3, 128.0, 126.6, 126.38, 126.35, 125.4, 121.7, 98.7, 73.9, 9.1, 1.2.

**1-(3,3-Dimethylbut-1-yn-1-yl)naphthalene (Scheme 1, 3l).**[20] According to the general procedure, the reaction of 1-naphthoic anhydride (0.2 mmol), 3,3-dimethylbut-1-yne (0.6 mmol, 3.0 equiv), $Pd(OAc)_2$ (0.006 mmol, 3 mol%), XantPhos (0.012 mmol, 6 mol%), and DMAP (0.3 mmol, 1.5 equiv) in dioxane (0.20 M) for 15 h at 160 °C, after work-up and chromatography (hexane/dichloromethane = 10/1 to 1/1) afforded the title compound in 74% yield (30.8 mg). Yellow solid. **$^1$H NMR (400 MHz, CDCl$_3$)** δ 8.33 (d, *J* = 8.3 Hz, 1 H), 7.83 (d, *J* = 8.0 Hz, 1 H), 7.77 (d, *J* = 8.3 Hz, 1 H), 7.62 (dd, $J^1$ = 7.1 Hz, $J^2$ = 1.2 Hz, 1 H), 7.58-7.54 (m, 1 H), 7.52-7.48 (m, 1 H), 7.40 (dd, $J^1$ = 8.3 Hz, $J^2$ = 7.1 Hz, 1 H), 1.44 (s, 9 H). **$^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$)** δ 133.6, 133.3, 130.0, 128.3, 128.0, 126.6, 126.4, 126.3, 125.3, 121.8, 103.9, 31.3, 28.5.

**Triisopropyl(naphthalen-1-ylethynyl)silane (Scheme 1, 3m).**[12] According to the general procedure, the reaction of 1-naphthoic anhydride (0.2 mmol), ethynyltriisopropylsilane (0.6 mmol, 3.0 equiv), Pd(OAc)$_2$ (0.006 mmol, 3 mol%), XantPhos (0.012 mmol, 6 mol%), and DMAP (0.3 mmol, 1.5 equiv) in dioxane (0.20 M) for 15 h at 160 °C, after work-up and chromatography (hexane/dichloromethane = 10/1 to 1/1) afforded the title compound in 87% yield (53.5 mg). Light yellow solid. **$^1$H NMR (400 MHz, CDCl$_3$)** *δ* 8.41 (d, *J* = 8.3 Hz, 1 H), 7.84 (t, *J* = 8.9 Hz, 2 H), 7.74 (dd, $J^1$ = 7.2 Hz, $J^2$ = 1.2 Hz, 1 H), 7.61-7.57 (m, 1 H), 7.54-7.50 (m, 1 H), 7.42 (dd, $J^1$ = 8.3 Hz, $J^2$ = 7.1 Hz, 1 H), 1.21-1.19 (m, 21 H). **$^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$)** *δ* 133.6, 133.2, 131.2, 128.9, 128.4, 127.0, 126.5, 126.4, 125.3, 121.3, 105.1, 95.9, 18.9, 11.5.

**2-(Phenylethynyl)naphthalene (Scheme 1, 3n).**[13] According to the general procedure, the reaction of 2-naphthoic anhydride (0.2 mmol), ethynylbenzene (0.6 mmol, 3.0 equiv), Pd(OAc)$_2$ (0.006 mmol, 3 mol%), XantPhos (0.012 mmol, 6 mol%), and DMAP (0.3 mmol, 1.5 equiv) in dioxane (0.20 M) for 15 h at 160 °C, after work-up and chromatography (hexane/dichloromethane = 10/1 to 1/1) afforded the title compound in 65% yield (29.5 mg). White solid. **$^1$H NMR (400 MHz, CDCl$_3$)** δ 8.06 (s, 1 H), 7.84-7.81 (m, 3 H), 7.60-7.58 (m, 3 H), 7.52-7.48 (m, 2 H), 7.39-7.35 (m, 3 H). **$^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$)** δ 133.1, 132.9, 131.8, 131.6, 128.6, 128.52, 128.45, 128.1, 127.9, 126.8, 126.7, 123.4, 120.7, 89.93, 89.87.

**2-((4-Methoxyphenyl)ethynyl)naphthalene (Scheme 1, 3o).**[12] According to the general procedure, the reaction of 2-naphthoic anhydride (0.2 mmol), 1-ethynyl-4-methoxybenzene (0.6 mmol, 3.0 equiv), Pd(OAc)$_2$ (0.006 mmol, 3 mol%), XantPhos (0.012 mmol, 6 mol%), and DMAP (0.3 mmol, 1.5 equiv) in dioxane (0.20 M) for 15 h at 160 °C, after work-up and chromatography (hexane/dichloromethane = 10/1 to 1/1) afforded the title compound in 61% yield (31.5 mg). White solid. **$^1$H NMR (400 MHz, CDCl$_3$)** δ 8.05 (s, 1 H), 7.84-7.80 (m, 3 H), 7.58 (dd, $J^1$ = 8.4 Hz, $J^2$ = 1.6 Hz, 1 H), 7.54 (d, $J$ = 8.8 Hz, 2 H), 7.51-7.47 (m, 2 H), 6.91 (d, $J$ = 8.8 Hz, 2 H), 3.84 (s, 3 H). **$^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$)** δ 159.8, 134.2, 133.24, 133.19, 132.8, 131.2, 128.6, 128.1, 127.9, 127.8, 126.6, 121.0, 115.5, 114.2, 89.9, 88.6, 55.4.

**Methyl 4-(naphthalen-2-ylethynyl)benzoate (Scheme 1, 3p).**[21] According to the general procedure, the reaction of 2-naphthoic anhydride (0.2 mmol), methyl 4-ethynylbenzoate (0.6 mmol, 3.0 equiv), Pd(OAc)$_2$ (0.006 mmol, 3 mol%), XantPhos (0.012 mmol, 6 mol%), and DMAP (0.3 mmol, 1.5 equiv) in dioxane (0.20 M) for 15 h at 160 °C, after work-up and chromatography (hexane/dichloromethane = 10/1 to 1/1) afforded the title compound in 76% yield (43.4 mg). White solid. **$^1$H NMR (400 MHz, CDCl$_3$)** δ 8.08 (s, 1 H), 8.05 (d, $J$ = 8.4 Hz, 2 H), 7.85-7.82 (m, 3 H), 7.65-7.62 (m, 2 H), 7.59 (dd, $J^1$ = 8.5 Hz, $J^2$ = 1.7 Hz, 1 H), 7.53-7.49 (m, 2 H), 3.94 (s, 3 H). **$^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$)** δ 166.7, 133.14, 133.09, 132.6, 132.0, 131.7, 129.7, 128.4, 128.3, 128.2, 128.0, 127.9, 127.1, 126.8, 120.1, 92.9, 89.1, 52.4.

**2-((4-Fluorophenyl)ethynyl)naphthalene (Scheme 1, 3q).**[10] According to the general procedure, the reaction of 2-naphthoic anhydride (0.2 mmol), 1-ethynyl-4-fluorobenzene (0.6 mmol, 3.0 equiv), Pd(OAc)$_2$ (0.006 mmol, 3 mol%), XantPhos (0.012 mmol, 6 mol%), and DMAP (0.3 mmol, 1.5 equiv) in dioxane (0.20 M) for 15 h at 160 °C, after work-up and chromatography (hexane/dichloromethane = 10/1 to 1/1) afforded the title compound in 70% yield (34.4 mg). White solid. **$^1$H NMR (400 MHz, CDCl$_3$)** δ 8.06 (s, 1 H), 7.85-7.81 (m, 3 H), 7.59-7.55 (m, 3 H), 7.52-7.50 (m, 2 H), 7.10-7.04 (m, 2 H). **$^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$)** δ 162.7 (d, $J$ = 249.7 Hz), 133.7, 133.6, 133.0 (d, $J$ = 18.5 Hz), 131.6, 128.5, 128.2, 127.9, 126.9, 126.7, 120.5, 119.5 (d, $J$ = 3.6 Hz), 115.9, 115.7, 89.6, 88.8. **$^{19}$F NMR (376 MHz, CDCl$_3$)** δ -110.80.

**2-((2-Chlorophenyl)ethynyl)naphthalene (Scheme 1, 3r).**[22] According to the general procedure, the reaction of 2-naphthoic anhydride (0.2 mmol), 1-chloro-2-ethynylbenzene (0.6 mmol, 3.0 equiv), $Pd(OAc)_2$ (0.006 mmol, 3 mol%), XantPhos (0.012 mmol, 6 mol%), and DMAP (0.3 mmol, 1.5 equiv) in dioxane (0.20 M) for 15 h at 160 °C, after work-up and chromatography (hexane/dichloromethane = 10/1 to 1/1) afforded the title compound in 60% yield (31.4 mg). White solid. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.01 (s, 1 H), 7.75-7.72 (m, 3 H), 7.54-7.50 (m, 2 H), 7.42-7.40 (m, 2 H), 7.37-7.35 (m, 1 H), 7.18-7.15 (m, 2 H). **$^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$)** δ 136.1, 134.5, 133.4, 133.1, 131.8, 129.5, 129.4, 128.5, 128.2, 128.0, 127.9, 127.0, 126.7, 126.6, 123.4, 120.3, 95.1, 86.6.

**Triisopropyl(naphthalen-2-ylethynyl)silane (Scheme 1, 3s).**[10] According to the general procedure, the reaction of 2-naphthoic anhydride (0.2 mmol), ethynyltriisopropylsilane (0.6 mmol, 3.0 equiv), $Pd(OAc)_2$ (0.006 mmol, 3 mol%), XantPhos (0.012 mmol, 6 mol%), and DMAP (0.3 mmol, 1.5 equiv) in dioxane (0.20 M) for 15 h at 160 °C, after work-up and chromatography (hexane/dichloromethane = 10/1 to 1/1) afforded the title compound in 81% yield (49.8 mg). White solid. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.02 (s, 1 H), 7.82-7.76 (m, 3 H), 7.54 (d, $J$ = 8.5 Hz, 1 H), 7.53-7.47 (m, 2 H), 1.19 (s, 21 H). **$^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$)** δ 133.1, 133.0, 132.0, 129.0, 128.0, 127.87, 127.85, 126.8, 126.6, 121.0, 107.6, 91.1, 18.9, 11.5.

**1-Methoxy-4-(phenylethynyl)benzene (Scheme 2, 3t).**[13] According to the general procedure, the reaction of 4-methoxybenzoic anhydride (0.2 mmol), ethynylbenzene (0.6 mmol, 3.0 equiv), $Pd(OAc)_2$ (0.006 mmol, 3 mol%), XantPhos (0.012 mmol, 6 mol%), and DMAP (0.3 mmol, 1.5 equiv) in dioxane (0.20 M) for 15 h at 160 °C, after work-up and chromatography (hexane/dichloromethane = 10/1 to 1/1) afforded the title compound in 61% yield (25.3 mg). White solid. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.56-7.48 (m, 4 H), 7.38-7.31 (m, 3 H), 6.91-6.88 (m, 2 H), 3.83 (s, 3 H). **$^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$)** δ 159.7, 133.2, 131.6, 128.4, 128.1, 123.7, 115.5, 114.1, 89.5, 88.2, 55.4.

**Methyl 4-(phenylethynyl)benzoate (Scheme 2, 3u).**[23] According to the general procedure, the reaction of 4-(methoxycarbonyl)benzoic anhydride (0.2 mmol), ethynylbenzene (0.6 mmol, 3.0 equiv), $Pd(OAc)_2$ (0.006 mmol, 3 mol%), XantPhos (0.012 mmol, 6 mol%), and DMAP (0.3 mmol, 1.5 equiv) in dioxane (0.20 M) for 15 h at 160 °C, after work-up and chromatography (hexane/dichloromethane = 10/1 to 1/1) afforded the title compound in 74% yield (34.8 mg). White solid. **$^1H$ NMR (400 MHz, $CDCl_3$)** δ 8.02 (d, *J* = 8.6 Hz, 2 H), 7.59 (d, *J* = 8.5 Hz, 2 H), 7.56-7.54 (m, 2 H), 7.38-7.35 (m, 3 H), 3.93 (s, 3 H). **$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)** δ 166.7, 131.9, 131.6, 129.7, 129.6, 128.9, 128.6, 128.1, 122.8, 92.5, 88.8, 52.4.

**1-Chloro-4-(phenylethynyl)benzene (Scheme 2, 3v).**[13] According to the general procedure, the reaction of 4-chlorobenzoic anhydride (0.2 mmol), ethynylbenzene (0.6 mmol, 3.0 equiv), $Pd(OAc)_2$ (0.006 mmol, 3 mol%), XantPhos (0.012 mmol, 6 mol%), and DMAP (0.3 mmol, 1.5 equiv) in dioxane (0.20 M) for 15 h at 160 °C, after work-up and chromatography (hexane/dichloromethane = 10/1 to 1/1) afforded the title compound in 66% yield (28.0 mg). Yellow solid. **$^1H$ NMR (400 MHz, $CDCl_3$)** δ 7.54-7.52 (m, 2 H), 7.47 (d, *J* = 8.5 Hz, 2 H), 7.37-7.32 (m, 5 H). **$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)** δ 134.4, 132.9, 131.7, 128.8, 128.6, 128.5, 123.0, 121.9, 90.4, 88.4.

**1-Chloro-3-(phenylethynyl)benzene (Scheme 2, 3w).**[13] According to the general procedure, the reaction of 3-chlorobenzoic anhydride (0.2 mmol), ethynylbenzene (0.6 mmol, 3.0 equiv), $Pd(OAc)_2$ (0.006 mmol, 3 mol%), XantPhos (0.012 mmol, 6 mol%), and DMAP (0.3 mmol, 1.5 equiv) in dioxane (0.20 M) for 15 h at 160 °C, after work-up and chromatography (hexane/dichloromethane = 10/1 to 1/1) afforded the title compound in 72% yield (30.5 mg). Yellow solid. **$^1H$ NMR (400 MHz, $CDCl_3$)** δ 7.58-7.52 (m, 3 H), 7.41-7.39 (m, 1 H), 7.34-7.32 (m, 3 H), 7.24-7.18 (m, 2 H). **$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)** δ 136.0, 133.3, 131.8, 129.39, 129.36, 128.8, 128.5, 126.6, 123.3, 123.0, 94.7, 86.3.

**1-Methyl-2-(phenylethynyl)benzene (Scheme 2, 3x).**[13] According to the general procedure, the reaction of 2-methylbenzoic anhydride (0.2 mmol), ethynylbenzene (0.6 mmol, 3.0 equiv), $Pd(OAc)_2$

(0.006 mmol, 3 mol%), XantPhos (0.012 mmol, 6 mol%), and DMAP (0.3 mmol, 1.5 equiv) in dioxane (0.20 M) for 15 h at 160 °C, after work-up and chromatography (hexane/dichloromethane = 10/1 to 1/1) afforded the title compound in 64% yield (24.6 mg). Yellow oil. **$^1$H NMR (400 MHz, CDCl$_3$)** δ 7.55-7.52 (m, 2 H), 7.51 (d, *J* = 7.5 Hz, 1 H), 7.38-7.31 (m, 3 H), 7.24-7.23 (m, 2 H), 7.21-7.15 (m, 1 H), 2.52 (s, 3 H). **$^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$)** δ 140.3, 132.0, 131.6, 129.6, 128.5, 128.4, 128.3, 125.7, 123.7, 123.1, 93.5, 88.5, 20.9.

**1-Fluoro-2-(phenylethynyl)benzene (Scheme 2, 3y).**[13] According to the general procedure, the reaction of 2-fluorobenzoic anhydride (0.2 mmol), ethynylbenzene (0.6 mmol, 3.0 equiv), Pd(OAc)$_2$ (0.006 mmol, 3 mol%), XantPhos (0.012 mmol, 6 mol%), and DMAP (0.3 mmol, 1.5 equiv) in dioxane (0.20 M) for 15 h at 160 °C, after work-up and chromatography (hexane/dichloromethane = 10/1 to 1/1) afforded the title compound in 69% yield (27.0 mg). Yellow oil. **$^1$H NMR (400 MHz, CDCl$_3$)** δ 7.60-7.52 (m, 3 H), 7.38-7.30 (m, 4 H), 7.13 (q, *J* = 8.0 Hz, 2 H). **$^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$)** δ 162.7 (d, $J^F$ = 251.5 Hz), 133.6, 131.8, 130.1 (d, $J^F$ = 7.8 Hz), 128.7, 128.5, 124.1 (d, $J^F$ = 3.8 Hz), 123.0, 115.7 (d, $J^F$ = 21.0 Hz), 112.0 (d, $J^F$ = 15.6 Hz), 94.5, 82.8. **$^{19}$F NMR (376 MHz, CDCl$_3$)** δ -109.80.

**4-(Phenylethynyl)-*N,N*-dipropylbenzenesulfonamide (Scheme 2, 3z).** According to the general procedure, the reaction of 4-(*N,N*-dipropylsulfamoyl)benzoic anhydride (0.2 mmol), ethynylbenzene (0.6 mmol, 3.0 equiv), Pd(OAc)$_2$ (0.006 mmol, 3 mol%), XantPhos (0.012 mmol, 6 mol%), and DMAP (0.3 mmol, 1.5 equiv) in dioxane (0.20 M) for 15 h at 160 °C, after work-up and chromatography (hexane/dichloromethane = 10/1 to 1/1) afforded the title compound in 57% yield (38.9 mg). *New compound*. Yellow solid. **$^1$H NMR (400 MHz, CDCl$_3$)** δ 7.79-7.77 (d, *J* = 8.5 Hz, 2 H), 7.64-7.62 (d, *J* = 8.5 Hz, 2 H), 7.56-7.53 (m, 2 H), 7.39-7.36 (m, 3 H), 3.11-3.07 (t, *J* = 7.6 Hz, 4 H), 1.60-1.50 (m, 4 H), 0.89-0.86 (t, *J* = 7.4 Hz, 6 H). **$^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$)** δ 139.5, 132.1, 131.9, 129.1, 128.6, 127.6, 127.1, 122.5, 92.7, 88.0, 50.0, 22.0, 11.3. **HRMS (ESI)** m/z calcd for $C_{20}H_{24}NO_2S$ (M+H)$^+$ 342.1522, found 342.1524.

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

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

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