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Palladacycle-Catalyzed Decarboxylative Coupling of Alkynyl Carboxylic Acids with Aryl Chlorides under Air

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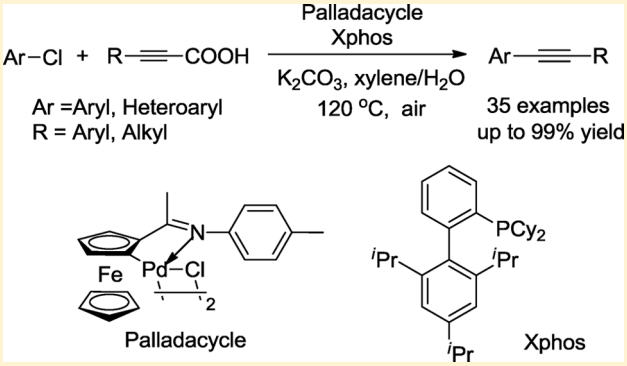
Supporting Information

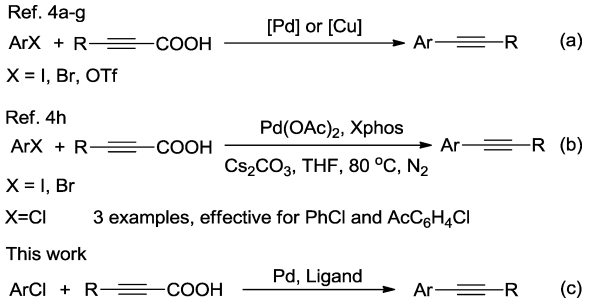
ABSTRACT: A highly efficient and practical protocol for palladacycle-catalyzed decarboxylative coupling of alkynyl carboxylic acids with aryl chlorides was developed. The reaction could proceed smoothly in air within 3 h under optimized reaction conditions (1 mol % of palladacycle, 4 mol % of Xphos, 2.0 equiv of K_2CO_3 in xylene/H_2O), affording the corresponding internal alkynes in mostly good to excellent yields. Remarkably, this result represents the first successful examples of this type of decarboxylative cross-coupling using electron-poor, electron-neutral and even inactive sterically hindered electron-rich aryl chlorides as the starting materials.



INTRODUCTION

The Sonogashira reaction as one of the most useful and reliable tools for the formation of C(sp)−C(sp^2) bonds[1] has been widely applied in the synthesis of pharmaceuticals, natural products, and advanced functional materials.[2] However, the Sonogashira coupling could not be applicable to the electron-poor terminal alkynes and typically requires copper salts as the cocatalyst, which would result in the homocoupling of terminal alkynes.[3] To overcome these drawbacks and limitations, decarboxylative coupling of alkynyl carboxylic acids with aryl halides as a new C(sp)−C(sp^2) bond-forming reaction has attracted much attention within recent years.[4] Typically, this new palladium- or copper-catalyzed reaction would take alkynyl carboxylic acids instead of terminal alkynes as the coupling partner. In 2008, Lee and co-workers introduced the first successful decarboxylative coupling of alkynyl carboxylic acids with aryl iodides or bromides using the Pd_2dba_3/dppf catalytic system.[4a] Since then, significant progress has been achieved by using palladium (e.g., Pd_2dba_3·$CHCl_3$, Pd_2dba_3, and Pd-$(PPh_3)_2Cl_2$) or copper (e.g., CuBr, CuI, and CuI/Fe$(acac)_3$) as the catalyst in Lee, Mao, You, and others' groups (Scheme 1a).[4b−g] However, the substrate scope in these reports is mainly limited to aryl iodides and bromides, and the decarboxylative coupling using more commercial available aryl chlorides as the starting material is still relatively rare. In 2010, Li and co-workers reported the first examples of decarboxylative coupling involving aryl chloride as the coupling partner with the aid of $Pd(OAc)_2$/Xphos (2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl) as the catalyst system.[4h] This reaction was effective for the more active electron-poor 4-chloroacetophenone and electron-neutral chlorobenzene. However, for inactive electron-rich substrate of 4-chloroanisole, only a relatively low yield (19%) was obtained (Scheme 1b). Therefore, a generally applicable catalytic system for aryl chlorides as a fascinating research area is still rich in challenges and opportunities (Scheme 1c).

Scheme 1. Decarboxylative Coupling of Alkynyl Carboxylic Acids with Aryl Halides



In recent years, our group focuses research interests on the application of a family of palladacyclic catalyst: cyclopalladated ferrocenylimines, which have exhibited high catalytic activity in various reactions (Figure 1).[5] Inspired by the previous

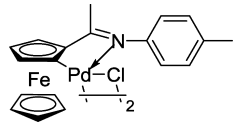


Figure 1. Palladacycle: cyclopalladated ferrocenylimine.

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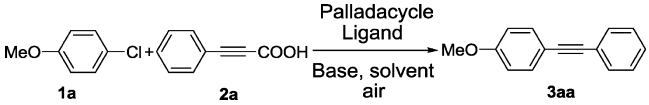
promising reports and our own results, herein we would attempt to explore the possibility of cyclopalladated ferrocenylimine-catalyzed decarboxylative coupling using aryl chlorides including inactive electron-rich aryl chlorides as the starting material, which would enhance the application scope of the decarboxylative coupling.

RESULTS AND DISCUSSION

Initially, the reaction of 4-chloroanisole (**1a**) and phenylpropiolic acid (**2a**) was selected as the model reaction and performed using Cs_2CO_3 as a base in THF in the presence of Xphos as the ligand at 80 °C (Li's reaction conditions[4h]), and a relatively low yield of 29% was obtained (Table 1, entry 1).

Table 1. Screening Optimal Conditions[a]



entry	ligand (mol %)	base	solvent	T (°C)	yield (%)
1[b]	Xphos (4)	Cs_2CO_3	THF	80	29
2	PPh_3 (4)	Cs_2CO_3	THF	80	<5
3	$^tBu_3P{\cdot}HBF_4$ (4)	Cs_2CO_3	THF	80	<5
4	Davephos (4)	Cs_2CO_3	THF	80	<5
5	Ruphos(4)	Cs_2CO_3	THF	80	15
6	Xphos (4)	Cs_2CO_3	toluene	120	63
7	Xphos (4)	Cs_2CO_3	xylene	120	68
8	Xphos (4)	Cs_2CO_3	xylene/H_2O 1.5:0.5	120	85
9	Xphos (4)	Cs_2CO_3	xylene/H_2O 1.0:1.0	120	90
10	Xphos (4)	Cs_2CO_3	xylene/H_2O 0.5:1.5	120	82
11	Xphos (4)	Cs_2CO_3	H_2O	120	<5
12	**Xphos (4)**	**K_2CO_3**	**xylene/H_2O 1.0:1.0**	**120**	**95**
13	Xphos (2)	K_2CO_3	xylene/H_2O 1.0:1.0	120	81
14	-	K_2CO_3	xylene/H_2O 1.0:1.0	120	<5
15	Xphos (4)	K_2CO_3	xylene/H_2O 1.0:1.0	80	<5
16[c]	Xphos (4)	K_2CO_3	xylene/H_2O 1.0:1.0	120	<5
17[d]	Xphos (4)	K_2CO_3	xylene/H_2O 1.0:1.0	120	68
18[e]	Xphos (4)	K_2CO_3	xylene/H_2O 1.0:1.0	120	21
19[f]	Xphos (4)	K_2CO_3	xylene/H_2O 1.0:1.0	120	18
20[g]	Xphos (4)	K_2CO_3	xylene/H_2O 1.0:1.0	120	<5
21[h]	Xphos (10)	K_2CO_3	xylene/H_2O 1.0:1.0	120	<5

[a]Reaction conditions: 4-chloroanisole (0.4 mmol), phenylpropiolic acid (0.5 mmol), palladacycle (1 mol %), ligand (4 mol %) and base (0.8 mmol) in solvent (2.0 mL) under air for 3 h. [b]For 12 h under nitrogen atmosphere. [c]Without palladium source. [d]$Pd(OAc)_2$ (2 mol %) was used instead of the palladacycle. [e]$PdCl_2$ (2 mol %) was used instead of the palladacycle. [f]Pd_2dba_3 (1 mol %) was used instead of the palladacycle. [g]Ni(dppe)Cl_2 (5 mol %) was used instead of the palladacycle. [h]CuI (5 mol %) was used instead of the palladacycle.

Subsequently, the effect of different other ligands such as PPh_3, $^tBu_3P{\cdot}HBF_4$, Davephos (2-dicyclohexylphosphino-2′-(*N*,*N*-dimethylamino)biphenyl), and Ruphos (2-dicyclohexylphosphino-2′,6′-diisopropoxy-1,1′-biphenyl) was also screened, and unfortunately, even lower yields than that of Xphos were observed (Table 1, entries 2−5). Then, solvents effect was also checked and fortunately, when the nonpolar solvents of toluene and xylene were employed, the yields could be enhanced to 63% and 68%, respectively (Table 1, entries 6 and 7). To our delight, the yields significantly changed with the addition of water to these catalytic systems (Table 1, entries 8−10). For example, when the ratios of xylene/H_2O were changed to 1.5:0.5, 1.0:1.0, and 0.5:1.5 the corresponding products were obtained in yields of 85%, 90%, and 82% (Table 1, entries 8−10). However, when the reaction was conducted in neat water, no product was observed (Table 1, entry 11). Obviously, xylene/H_2O (1.0:1.0) as the solvent is best choice for this reaction (Table 1, entries 8−11). Subsequently, K_2CO_3 was used as a base instead of Cs_2CO_3, and the isolated yield was even up to 95% (Table 1, entry 12). When the reaction was performed at a lower ligand loading of 2 mol %, the relatively lower yield of 81% was obtained (Table 1, entry 13). However, the reaction under ligand-free conditions or at a lower temperature of 80 °C did not occur at all, which indicated both the ligand and temperature played essential role in this reaction (Table 1, entries 14 and 15). Finally, some controlling experiments on palladium source were also performed (Table 1, entries 16−21). Under the palladium-free conditions, the reaction did not take place (Table 1, entry 16). Some commercially available palladium catalysts (e.g., $Pd(OAc)_2$, $PdCl_2$, and Pd_2dba_3) were also evaluated in this decarboxylative coupling, and the desired coupling products were obtained in relatively lower yields of 68%, 21%, and 18%, respectively (Table 1, entries 17−19). However, other metal catalysts such as Ni(dppe)Cl_2 and CuI did not exhibit catalytic activity in this reaction (Table 1, entries 20 and 21).

With the optimized conditions in hand, the substrate scope of aryl chlorides was then explored, and the results are summarized in Table 2. Generally, electronic effect had no significant influence on this decarboxylative coupling, and the reactions of electron-rich, electron-neutral, and electron-poor aryl chlorides could afford the corresponding products in good to excellent yields (Table 2, entries 1−20). It was noteworthy that the sterically hindered substrates (**1e−i**) also successfully coupled with phenylpropiolic acid (**2a**) in excellent isolated yield (Table 2, entries 4−8). Especially, even for the substrates bearing the two *ortho* sterically hindered substituents such as 2-chloro-*m*-xylene (**1h**) and 2-chloromesitylene (**1i**), the corresponding products could also be afforded in up to high yields of 90% and 89%, respectively (Table 2, entries 7 and 8). Moreover, base-sensitive groups (e.g., $COOCH_3$, CH_3CO, CN, and CHO) or other functional groups such as NO_2 and CF_3 could be well tolerated in this decarboxylative coupling (Table 2, entries 12−18). In addition, the coupling of aromatic heterocyclic chlorides such as 3-chloropyridine (**1t**) and 2-chlorothiophene (**1u**) could also proceed smoothly, affording the corresponding internal alkynes in high yields of 87% and 95%, respectively (Table 2, entries 19 and 20). However, when the substrate bore a hydroxyl group such as 4-chlorophenol (**1v**), the reaction failed to give the desired product (Table 2, entry 21).

Subsequently, the scope of arylpropiolic acids was also explored, and the results in Table 3 indicated that electronic or steric effect has no crucial influence on this decarboxylative coupling. For example, arylpropiolic acids bearing either electron-donating or electron-withdrawing groups on the aryl ring moiety could be efficiently converted into the corresponding products in moderate to good yields (Table 3, entries 1−5). Moreover, the yield of sterically hindered *o*-methylphenylpropiolic acid (**2c**) with 4-chloroanisole (**1a**) was up to 87% (Table 3, entry 2).

Finally, the decarboxylative coupling of aliphatic propiolic acids was also investigated, and both 2-octynoic acid (**2g**) and

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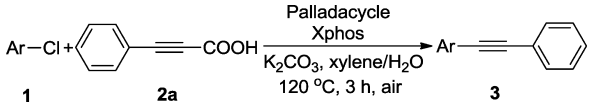
Table 2. Decarboxylative Coupling of Phenylpropiolic Acid with Aryl Chlorides[a]



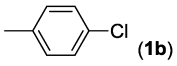
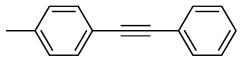
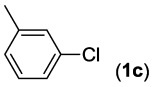
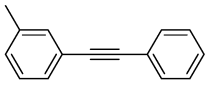
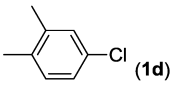
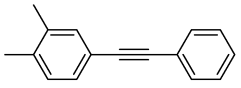
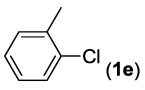
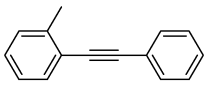
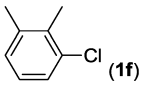
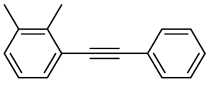
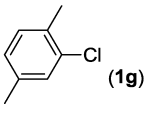
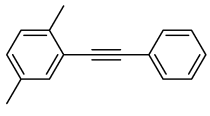
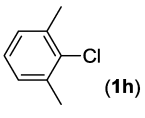
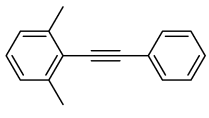
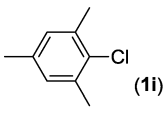
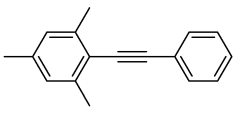
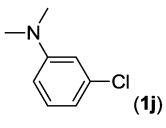
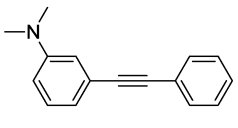
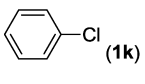
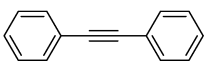
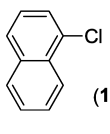
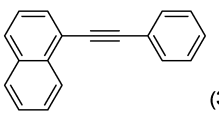
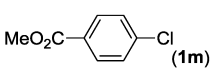
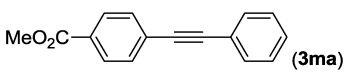
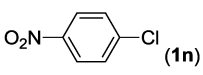
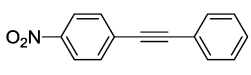
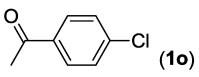
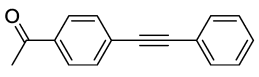
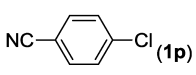
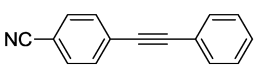
Entry	Aryl chloride	Product	Yield (%)
1	 (1b)	 (3ba)	92
2	 (1c)	 (3ca)	89
3	 (1d)	 (3da)	91
4	 (1e)	 (3ea)	88
5	 (1f)	 (3fa)	91
6	 (1g)	 (3ga)	95
7	 (1h)	 (3ha)	90
8[b]	 (1i)	 (3ia)	89
9	 (1j)	 (3ja)	89
10	 (1k)	 (3ka)	94
11	 (1l)	 (3la)	95
12	 (1m)	 (3ma)	84
13	 (1n)	 (3na)	99
14	 (1o)	 (3oa)	89
15	 (1p)	 (3pa)	92

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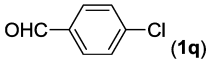
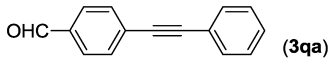
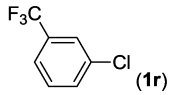
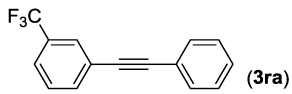
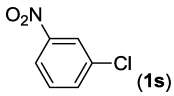
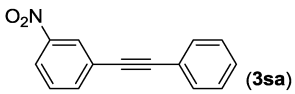
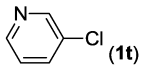
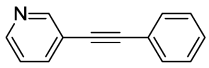
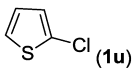
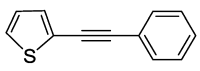
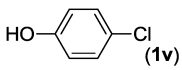
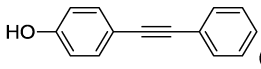
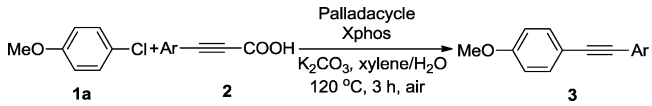
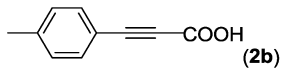
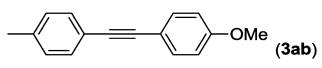
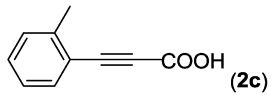
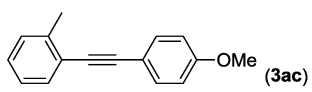
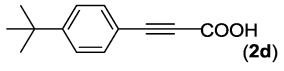
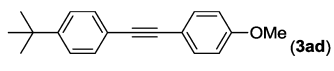
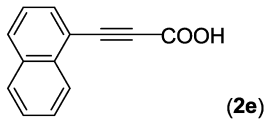
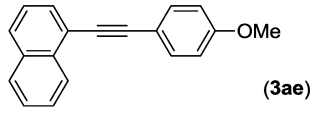
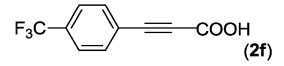
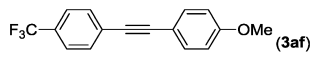
Table 2. continued

Entry	Aryl chloride	Product	Yield (%)
16	 (1q)	 (3qa)	90
17	 (1r)	 (3ra)	93
18	 (1s)	 (3sa)	91
19	 (1t)	 (3ta)	87
20	 (1u)	 (3ua)	95
21	 (1v)	 (3va)	<5

[a]Reaction conditions: aryl chlorides (0.4 mmol), phenylpropiolic acid (0.5 mmol), palladacycle (1 mol %), Xphos (4 mol %) and K_2CO_3 (0.8 mmol) in xylene/H_2O (1.0 mL/1.0 mL) at 120 °C under air for 3 h. [b]Xylene (2.0 mL) as the solvent under nitrogen atmosphere.

Table 3. Decarboxylative Coupling of Aryl Propiolic Acids with 4-Chloroanisole[a]



Entry	Aryl propiolic acid	Product	Yield(%)
1	 (2b)	 (3ab)	92
2	 (2c)	 (3ac)	87
3	 (2d)	 (3ad)	88
4	 (2e)	 (3ae)	85
5[b]	 (2f)	 (3af)	70

[a]Reaction conditions: 4-chloroanisole (0.4 mmol), arylpropiolic acid (0.5 mmol), palladacycle (1 mol %), Xphos (4 mol %), and K_2CO_3 (0.8 mmol) in xylene/H_2O (1.0 mL/1.0 mL) at 120 °C under air for 3 h. [b]Xylene (2.0 mL) as the solvent under nitrogen atmosphere.

2-butynoic acid (**2h**) could be efficiently coupled with aryl chlorides, affording the corresponding products in moderate to excellent yields (Table 4). It is worth noting that both electron-rich and electron-deficient aryl chlorides could successfully undergo the decarboxylative coupling, which indicates that the electronic effect of aryl chlorides has no obvious influence on

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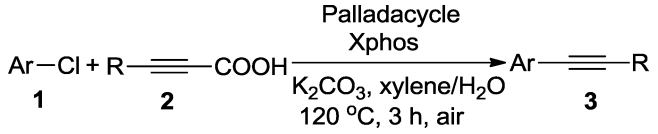
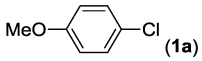
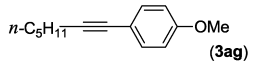
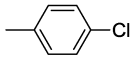
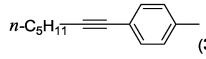
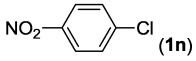
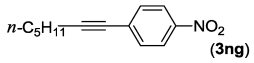
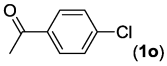
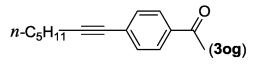
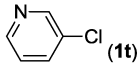
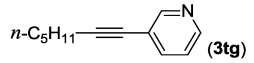
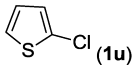
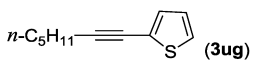
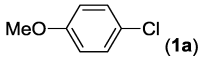
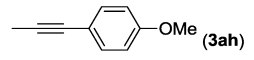
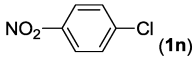
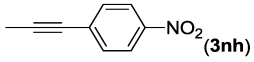
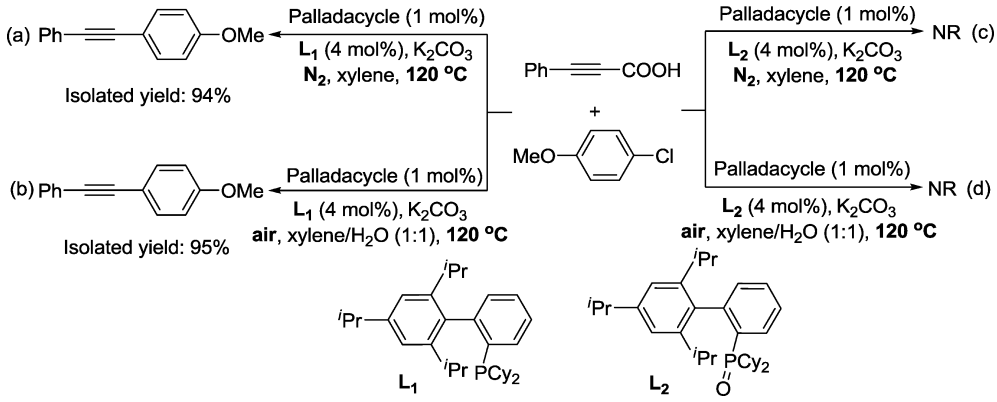
Table 4. Decarboxylative Coupling of Aryl Chlorides with Aliphatic Propiolic Acids[a]



Entry	Aryl chloride	R	Product	Yield(%)
1	 (1a)	*n*-C_5H_{11} (2g)	 (3ag)	91
2	 (1b)	*n*-C_5H_{11} (2g)	 (3bg)	93
3	 (1n)	*n*-C_5H_{11} (2g)	 (3ng)	94
4	 (1o)	*n*-C_5H_{11} (2g)	 (3og)	98
5	 (1t)	*n*-C_5H_{11} (2g)	 (3tg)	91
6	 (1u)	*n*-C_5H_{11} (2g)	 (3ug)	81
7	 (1a)	CH_3 (2h)	 (3ah)	52
8	 (1n)	CH_3 (2h)	 (3nh)	80

[a]Reaction conditions: aryl chloride (0.4 mmol), aliphatic propiolic acid (0.5 mmol), palladacycle (1 mol %), Xphos (4 mol %), and K_2CO_3 (0.8 mmol) in xylene/H_2O (1.0 mL/1.0 mL) at 120 °C under air for 3 h.

Scheme 2. Controlling Experiments for Mechanistic Studies



this reaction (Table 4, entries 1–4, 7, and 8). Moreover, aromatic heterocyclic chlorides such as 3-chloropyridine (**1t**) and 2-chlorothiophene (**1u**) were also reactive partners in this coupling (Table 4, entries 5 and 6).

To reveal the real ligand and the role of the air in this reaction, some controlling experiments for mechanistic studies were carried out and are presented in Scheme 2. First, we performed the reaction in xylene under nitrogen atmosphere using the alkyl phosphine ligand (L_1) as the ligand, and to our surprise, the isolated yield was up to 94% (Scheme 2a), which was almost the same as that in the mixed solvent of xylene/water under air (Scheme 2b). As we know, the alkylphosphine ligand (L_1) could easily be oxidized to the phosphine oxide (L_2) in air. Therefore, we tried to utilize the phosphine oxide (L_2) as the ligand directly, but unfortunately, the reaction did not occur at all either in xylene under nitrogen atmosphere or in the mixed solvent of xylene/water under air (Scheme 2c and d). These discoveries indicated that the real ligand must be the alkylphosphine ligand (L_1), and this catalytic system should be performed under oxidant (including air)-free conditions.

On the basis of the above-mentioned results, a possible mechanism of palladacycle-catalyzed decarboxylative coupling

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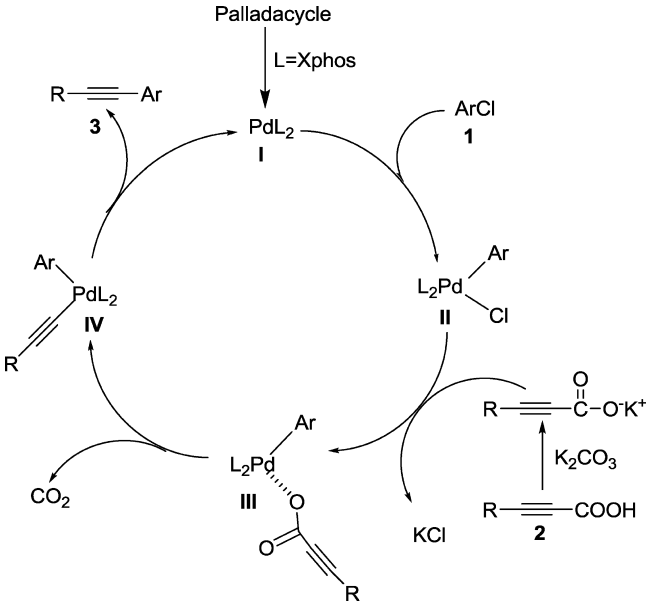
reaction is outlined in Scheme 3. In 2010, our previous report has indicated that palladacycle was just a reservoir of

Scheme 3. Proposed Mechanism of Palladacycle-Catalyzed Decarboxylative Coupling Reaction



catalytically active Pd(0) species in the coupling reaction.[5a] Thus, the first step would be the release of Pd(0) species from palladacycle to form the catalytically active Pd(0)L_2 (**I**) with the assist of the alkyl phosphine ligand. Then, the oxidative addition of aryl chloride (**1**) to Pd(0)L_2 would take place to form the intermediate **II**. Subsequently, the ligand-exchange reaction between intermediate **II** and alkynyl carboxylic acid anion which was generated by the reaction of alkynyl acids and K_2CO_3 could occur to afford intermediate **III**. After the intermediate **III** underwent the decarboxylative reaction to release one molecular CO_2 to form the intermediate **IV**, the reductive elimination of the intermediate **IV** would afford the corresponding products (**3**) and regenerate the catalytically active catalyst Pd(0)L_2 to fulfill the catalytic cycle.

CONCLUSIONS

In summary, we have developed a highly efficient and generally applicable protocol for the decarboxylative coupling of alkynyl carboxylic acids with aryl chlorides under the catalyst system of cyclopalladated ferrocenylimine (1 mol %)/Xphos (4 mol %). It is noteworthy that the scope of the substrate could be extended to electron-poor, electron-neutral, and even inactive sterically hindered electron-rich aryl chlorides and the reaction could be operated under air, all of which would make the decarboxylative coupling more economical and practical in the industrial process in the future.

EXPERIMENTAL SECTION

General Methods. ^{1}H and ^{13}C NMR spectra were recorded with $CDCl_3$ as the solvent and TMS as an internal standard. The cyclopalladated ferrocenylimine was synthesized according to the reported literature.[5b] The other chemicals were bought from commercial sources and used as received unless otherwise noted.

General Procedure for the Palladacycle-Catalyzed Decarboxylative Coupling of Alkynyl Carboxylic Acids with Aryl Chlorides. Aryl chloride (0.4 mmol), alkynyl carboxylic acid (0.5 mmol), K_2CO_3 (2 equiv), palladacycle (1 mol %), and Xphos (4 mol %) were added to a 10 mL round-bottomed flask, and then a mixed solvent of 1.0 mL of xylene and 1.0 mL of H_2O was added. The mixture was stirred at 120 °C for 3 h under air. After the reaction was complete, the mixture was washed with brine and extracted with ethyl acetate three times. The combined organic layer was dried with anhydrous Na_2SO_4 and evaporated in vacuum. The crude product was purified by flash chromatography on silica gel using hexane or hexane/ethyl acetate (1:10) as the eluent to give the pure product.

1-Methoxy-4-(phenylethynyl)benzene (**3aa**):[6] light yellow solid (79 mg, 95%); mp 57−59 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.80 (s, 3H), 6.86 (d, J = 8.7 Hz, 2H), 7.30−7.32 (m, 3H), 7.46 (d, J = 8.8 Hz, 2H), 7.49−7.51 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.3, 88.1, 89.4, 114.0, 115.4, 123.7, 128.0, 128.3, 131.5, 133.1, 159.7.

1-Methyl-4-(phenylethynyl)benzene (**3ba**):[7] white solid (70 mg, 92%); mp 68−70 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.38 (s, 3H), 7.16 (d, J = 7.9 Hz, 2H), 7.33−7.35 (m, 3H), 7.44 (d, J = 8.1 Hz, 2H), 7.53−7.55 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 88.7, 89.6, 120.2, 123.5, 128.1, 128.3, 129.1, 131.5, 131.5, 138.4.

1-Methyl-3-(phenylethynyl)benzene (**3ca**):[7] colorless oil (68 mg, 89%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.38 (s, 3H), 7.17 (d, J = 7.56 Hz, 1H), 7.26 (t, J = 7.6 Hz, 1H), 7.35−7.40 (m, 5H), 7.55−7.57 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 89.1, 89.6, 123.1, 123.4, 128.2, 128.2, 128.3, 128.7, 129.1, 131.6, 132.2, 138.0.

1,2-Dimethyl-4-(phenylethynyl)benzene (**3da**):[8] white solid (75 mg, 91%); mp 61−62 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.28 (s, 3H), 2.29 (s, 3H), 7.12 (d, J = 7.7 Hz, 1H), 7.30 (d, J = 7.8 Hz, 1H), 7.32−7.37 (m, 4H), 7.53−7.55 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.6, 19.8, 88.5, 89.7, 120.5, 123.6, 128.0, 128.3, 129.1, 129.7, 131.6, 132.7, 136.7, 137.2.

1-Methyl-2-(phenylethynyl)benzene (**3ea**):[7] colorless oil (68 mg, 88%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.55 (s, 3H), 7.17−7.21 (m, 1H), 7.25 (d, J = 4.4 Hz, 2H), 7.36−7.39 (m, 3H), 7.51−7.57 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 88.4, 93.4, 123.1, 123.6, 125.6, 128.2, 128.3, 128.4, 129.5, 131.6, 131.9, 140.2.

1,2-Dimethyl-3-(phenylethynyl)benzene (**3fa**):[7] colorless oil (75 mg, 91%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.32 (s, 3H), 2.49 (s, 3H), 7.07−7.15 (m, 2H), 7.34−7.41 (m, 4H), 7.55−7.57 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.5, 20.4, 89.1, 92.7, 123.1, 123.7, 125.4, 128.1, 128.4, 129.8, 130.0, 131.5, 136.8, 138.6.

1,4-Dimethyl-2-(phenylethynyl)benzene (**3ga**):[9] light yellow solid (78 mg, 95%); mp 77−79 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.34 (s, 3H), 2.51 (s, 3H), 7.07 (d, J = 7.8 Hz, 1H), 7.15 (d, J = 7.8 Hz, 1H), 7.34−7.40 (m, 4H), 7.55−7.58 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.3, 20.8, 88.6, 93.0, 122.8, 123.7, 128.1, 128.4, 129.3, 129.4, 131.5, 132.3, 135.1, 137.1.

1,3-Dimethyl-2-(phenylethynyl)benzene (**3ha**):[10] colorless oil (74 mg, 90%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.56 (s, 6H), 7.10−7.16 (m, 3H), 7.37−7.39 (m, 3H), 7.57−7.59 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 87.1, 97.8, 122.9, 123.8, 126.7, 127.7, 128.0, 128.3, 131.3, 140.2.

1,3,5-Trimethyl-2-(phenylethynyl)benzene (**3ia**):[4b] colorless oil (79 mg, 89%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.33 (s, 3H), 2.51 (s, 6H), 6.92 (s, 2H), 7.34−7.40 (m, 3H), 7.55−7.58 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0, 21.3, 87.3, 97.0, 120.0, 124.0, 127.6, 127.9, 128.3, 131.3, 137.7, 140.1.

N,N-Dimethyl-3-(phenylethynyl)aniline (**3ja**):[11] colorless oil (79 mg, 89%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.97 (s, 6H), 6.71−6.74 (m, 1H), 6.92 (d, J = 7.4 Hz, 2H), 7.22 (t, J = 7.7 Hz, 1H), 7.32−7.35 (m, 3H), 7.54−7.56 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.4, 88.2, 90.3, 112.8, 115.2, 119.9, 123.4, 123.5, 128.0, 128.2, 129.0, 131.5, 150.3.

1,2-Diphenylethyne (**3ka**):[7] white solid (67 mg, 94%); mp 60−62 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.40 (m, 6H), 7.56−7.58 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 89.4, 123.3, 128.3, 128.4, 131.6.

1-(Phenylethynyl)naphthalene (**3la**):[12] colorless oil (87 mg, 95%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33−7.37 (m, 3H), 7.40−7.52 (m, 2H), 7.56−7.65 (m, 3H), 7.85 (d, J = 7.1 Hz, 1H), 7.80−7.84 (m, 2H), 8.44 (d, J = 8.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 87.6,

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94.4, 121.0, 123.5, 125.3, 126.3, 126.5, 126.8, 128.4, 128.4, 128.5, 128.8, 130.4, 131.7, 133.3, 133.3.

Methyl 4-(phenylethynyl)benzoate (**3ma**):[4b] light yellow solid (79 mg, 84%); mp 120−122 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.93 (s, 3H), 7.36 (t, J = 4.0 Hz, 3H), 7.53−7.56 (m, 2H), 7.59 (d, J = 8.3 Hz, 2H), 8.02 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.2, 88.5, 92.3, 122.6, 127.9, 128.4, 128.7, 129.4, 129.4, 131.4, 131.6, 166.5.

1-Nitro-4-(phenylethynyl)benzene (**3na**):[13] light yellow solid (88 mg, 99%); mp 114−116 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39−7.41 (m, 3H), 7.56−7.59 (m, 2H), 7.65−7.68 (m, 2H), 8.20−8.23 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 87.6, 94.7, 122.1, 123.6, 128.6, 129.3, 130.3, 131.9, 132.3, 147.0.

1-[4-(Phenylethynyl)phenyl]ethanone (**3oa**):[14] yellow solid (78 mg, 89%); mp 94−96 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.60 (s, 3H), 7.35−7.37 (m, 3H), 7.54−7.56 (m, 2H), 7.60 (d, J = 8.3 Hz, 2H), 7.93 (d, J = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.6, 88.6, 92.7, 122.6, 128.2, 128.4, 128.8, 131.7, 131.7, 136.2, 197.3.

4-(Phenylethynyl)benzonitrile (**3pa**):[14] yellow solid (75 mg, 92%); mp 102−103 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37−7.38 (m, 3H), 7.53−7.55 (m, 2H), 7.58−7.64 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 87.8, 93.8, 111.5, 118.6, 122.3, 128.3, 128.6, 129.2, 131.8, 132.1, 132.1.

4-(Phenylethynyl)benzaldehyde (**3qa**):[15] yellow solid (74 mg, 90%); mp 96−98 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.38 (m, 3H), 7.54−7.57 (m, 2H), 7.66 (d, J = 8.2 Hz, 2H), 7.86 (d, J = 8.2 Hz, 2H), 10.0 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 88.5, 93.4, 122.5, 128.5, 129.0, 129.5, 129.6, 131.8, 132.1, 135.4, 191.4.

1-(Phenylethynyl)-3-(trifluoromethyl)benzene (**3ra**):[16] colorless oil (92 mg, 93%); ^{1}H NMR (400 MHz, $CDCl_3$) 7.39 (t, J = 2.92 Hz, 3H), 7.47−7.51 (m, 1H), 7.56−7.60 (m, 3H), 7.71 (d, J = 7.6 Hz, 2H), 7.82 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 88.2, 91.3, 123.0, 124.2 (q, J = 270.8 Hz), 124.7, 125.2 (q, J = 3.7 Hz), 128.8 (q, J = 3.7 Hz), 128.9, 129.2, 129.3, 131.4 (q, J = 32.0 Hz), 132.1, 135.1.

1-Nitro-3-(phenylethynyl)benzene (**3sa**):[7] light yellow solid (81 mg, 91%); mp 68−70 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38−7.40 (m, 3H), 7.51−7.57 (m, 3H), 7.82 (d, J = 7.72 Hz, 1H), 8.16−8.19 (m, 1H), 8.37 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 86.7, 91.7, 122.0, 122.7, 125.0, 126.2, 128.3, 128.9, 129.2, 131.6, 137.0, 147.9.

3-(Phenylethynyl)pyridine (**3ta**):[4b] colorless oil (62 mg, 87%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26−7.29 (m, 1H), 7.36−7.37 (m, 3H), 7.53−7.56 (m, 2H), 7.79−7.81 (m, 1H), 8.54 (d, J = 3.8 Hz, 1H), 8.77 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 85.9, 92.6, 120.5, 122.5, 123.0, 128.4, 128.8, 131.7, 138.4, 148.5, 152.2.

2-(Phenylethynyl)thiophene (**3ua**):[4b] light yellow solid (70 mg, 95%); mp 48−50 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02−7.05 (m, 1H), 7.30−7.32 (m, 2H), 7.37−7.38 (m, 3H), 7.55 (d, J = 3.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 82.7, 93.1, 123.0, 123.4, 127.2, 127.3, 128.5, 128.5, 131.5, 132.0.

1-Methoxy-4-(4-tolylethynyl)benzene (**3ab**):[17] light yellow solid (82 mg, 92%); mp 118−120 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.36 (s, 3H), 3.82 (s, 3H), 6.86 (d, J = 8.8 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 7.40 (d, J = 8.1 Hz, 2H), 7.45 (d, J = 8.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 55.3, 88.2, 88.7, 114.0, 115.6, 120.5, 129.1, 131.3, 133.0, 138.0, 159.5.

1-[(4-Methoxyphenyl)ethynyl]-2-methylbenzene (**3ac**):[18] light yellow solid (77 mg, 87%); mp 74−75 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.52 (s, 3H), 3.82 (s, 3H), 6.89 (d, J = 8.8 Hz, 2H), 7.14−7.25 (m, 3H), 7.48−7.50 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 55.4, 87.1, 93.4, 114.1, 115.8, 123.4, 125.6, 128.0, 129.5, 131.7, 133.0, 140.0, 160.0.

1-tert-Butyl-4-[(4-methoxyphenyl)ethynyl]benzene (**3ad**):[19] light yellow solid (92 mg, 88%); mp 118−120 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32 (s, 9H), 3.82 (s, 3H), 6.87 (d, J = 8.8 Hz, 2H), 7.35 (d, J = 8.4 Hz, 2H), 7.43−7.47 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.2, 34.8, 55.3, 88.2, 88.7, 114.0, 115.7, 120.6, 125.3, 131.2, 133.0, 151.2, 160.0.

1-[(4-Methoxyphenyl)ethynyl]naphthalene (**3ae**):[20] light yellow oil (87 mg, 85%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.86 (s, 3H), 6.95 (d, J = 8.8 Hz, 2H), 7.45−7.49 (m, 1H), 7.53−7.57 (m, 1H), 7.60−7.63 (m, 3H), 7.77 (d, J = 6.8 Hz, 1H), 7.83−7.89 (m, 2H), 8.47 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.4, 86.3, 94.4, 114.1, 115.6, 121.3, 125.3, 126.3, 126.4, 126.7, 128.3, 128.4, 130.1, 133.2, 133.3, 159.8.

1-Methoxy-4-[[4-(trifluoromethyl)phenyl]ethynyl]benzene (**3af**):[21] yellow solid (78 mg, 70%); mp 113−115 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.83 (s, 3H), 6.88−6.90 (m, 2H), 7.47−7.49 (m, 2H), 7.56−7.61 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.3, 86.9, 92.0, 114.2, 114.7, 124.0 (q, J = 270.4 Hz), 125.3 (q, J = 3.8 Hz), 127.5, 129.6 (q, J = 32.4 Hz), 131.6, 133.3, 160.1.

1-(Hept-1-ynyl)-4-methoxybenzene (**3ag**):[4b] colorless oil (73 mg, 91%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92 (t, J = 7.1 Hz, 3H), 1.31−1.46 (m, 4H), 1.56−1.63 (m, 2H), 2.38 (t, J = 7.1 Hz, 2H), 3.78 (s, 3H), 6.80 (d, J = 8.7 Hz, 2H), 7.32 (d, J = 8.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 19.4, 22.3, 28.6, 31.2, 55.3, 80.2, 88.8, 113.8, 116.3, 132.9, 159.0.

1-(Hept-1-ynyl)-4-methylbenzene (**3bg**):[4b] colorless oil (69 mg, 93%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92 (t, J = 7.2 Hz, 3H), 1.32−1.48 (m, 4H), 1.58−1.65 (m, 2H), 2.33 (s, 3H), 2.40 (t, J = 7.1 Hz, 2H), 7.09 (d, J = 7.9 Hz, 2H), 7.30 (d, J = 7.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 19.4, 21.4, 22.3, 28.6, 31.2, 80.6, 89.7, 121.1, 129.0, 131.4, 137.4.

1-(Hept-1-ynyl)-4-nitrobenzene (**3ng**):[22] colorless oil (82 mg, 94%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.91 (t, J = 7.0 Hz, 3H), 1.30−1.45 (m, 4H), 1.57−1.64 (m, 2H), 2.42 (t, J = 7.1 Hz, 2H), 7.49 (d, J = 8.4 Hz, 2H), 8.12 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 19.5, 22.2, 28.1, 31.1, 79.3, 96.8, 123.5, 131.2, 132.2, 146.6.

1-[4-(Hept-1-ynyl)phenyl]ethanone (**3og**):[4b] colorless oil (84 mg, 98%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (t, J = 7.1 Hz, 3H), 1.30−1.45 (m, 4H), 1.56−1.63 (m, 2H), 2.40 (t, J = 7.1 Hz, 2H), 2.55 (s, 3H), 7.43 (d, J = 8.2 Hz, 2H), 7.84 (d, J = 8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 19.5, 22.2, 26.6, 28.3, 31.1, 80.1, 94.5, 128.2, 129.2, 131.6, 135.6, 197.4.

3-(Hept-1-ynyl)pyridine (**3tg**):[4b] colorless oil (63 mg, 91%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.93 (t, J = 7.1 Hz, 3H), 1.32−1.47 (m, 4H), 1.58−1.66 (m, 2H), 2.42 (t, J = 7.1 Hz, 2H), 7.18−7.22 (m, 1H), 7.65−7.67 (m, 1H), 8.47 (dd, J = 1.2, 4.7 Hz, 1H), 8.62 (d, J = 1.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 19.4, 22.2, 28.3, 31.1, 94.1, 121.2, 122.9, 138.4, 147.9, 152.3.

2-(Hept-1-ynyl)thiophene (**3ug**):[4b] colorless oil (58 mg, 81%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92 (t, J = 7.1 Hz, 3H), 1.31−1.46 (m, 4H), 1.57−1.64 (m, 2H), 2.42 (t, J = 7.1 Hz, 2H), 6.92−6.94 (m, 1H), 7.11−7.16 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 19.7, 22.3, 28.3, 31.2, 73.7, 94.6, 124.3, 125.8, 126.8, 130.9.

1-Methoxy-4-(prop-1-ynyl)benzene (**3ah**):[4e] colorless oil (30 mg, 52%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.05 (s, 3H), 3.82 (s, 3H), 6.83 (d, J = 8.7 Hz, 2H), 7.35 (d, J = 8.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 4.3, 55.3, 79.4, 84.1, 113.9, 116.2, 132.8, 159.0.

1-Nitro-4-(prop-1-ynyl)benzene (**3nh**):[23] yellow solid (52 mg, 80%); mp 103−104 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.10 (s, 3H), 7.50 (d, J = 8.7 Hz, 2H), 8.15 (d, J = 8.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 4.9, 78.9, 92.6, 123.9, 125.3, 130.0, 132.6.

■ ASSOCIATED CONTENT

Supporting Information

Copies of NMR spectra for all the compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) For selected reviews on Sonogashira reactions, see: (a) Sonogashira, K. *J. Organomet. Chem.* **2002**, *653*, 46−49. (b) Negishi, E.-I.; Anastasia, L. *Chem. Rev.* **2003**, *103*, 1979−2017. (c) Nicolaou, K. C.; Bulger, P. G.; Sarlah, D. *Angew. Chem., Int. Ed.* **2005**, *44*, 4442−4489. (d) Chinchilla, R.; Nájera, C. *Chem. Rev.* **2007**, *107*, 874−922. (e) Tykwinski, R. R. *Angew. Chem., Int. Ed.* **2003**, *42*, 1566−1568.

(2) For selected papers, see: (a) Kim, T.-H.; Swager, T. M. *Angew. Chem., Int. Ed.* **2003**, *42*, 4803−4806. (b) Liu, J.-Z.; Lam, J. W. Y.; Tang, B. Z. *Chem. Rev.* **2009**, *109*, 5799−5867. (c) Nicolaou, K. C.; Zipkin, R. E.; Dolle, R. E.; Harris, B. D. *J. Am. Chem. Soc.* **1984**, *106*, 3548−3551. (d) Rakshit, S.; Patureau, F. W.; Glorius, F. *J. Am. Chem. Soc.* **2010**, *132*, 9585−9587.

(3) (a) Park, J.; Park, E.; Kim, A.; Park, S.-A.; Lee, Y.; Chi, K. W.; Jung, Y. H.; Kim, I. S. *J. Org. Chem.* **2011**, *76*, 2214−2219. (b) Kim, Y.; Park, A.; Park, K.; Lee, S. *Tetrahedron Lett.* **2011**, *52*, 1766−1769.

(4) (a) Moon, J.; Jeong, M.; Nam, H.; Ju, J.; Moon, J. H.; Jung, H. M.; Lee, S. *Org. Lett.* **2008**, *10*, 945−948. (b) Moon, J.; Jang, M.; Lee, S. *J. Org. Chem.* **2009**, *74*, 1403−1406. (c) Kim, H.; Lee, P. H. *Adv. Synth. Catal.* **2009**, *351*, 2827−2832. (d) Zhao, D.-B.; Gao, C.; Su, X.-Y.; He, Y.-Q.; You, J.-S.; Xue, Y. *Chem. Commun.* **2010**, *46*, 9049−9051. (e) Pan, D.-L.; Zhang, C.; Ding, S.-T.; Jiao, N. *Eur. J. Org. Chem.* **2011**, 4751−4755. (f) Li, T.-Y.; Qu, X.-M.; Zhu, Y.; Sun, P.; Yang, H.-L.; Shan, Y.-Q.; Zhang, H.-X.; Liu, D.-F.; Zhang, X.; Mao, J.-C. *Adv. Synth. Catal.* **2011**, *353*, 2731−2738. (g) Qu, X.-M.; Li, T.-Y.; Sun, P.; Zhu, Y.; Yang, H.-L.; Mao, J.-C. *Org. Biomol. Chem.* **2011**, *9*, 6938−6942. (h) Zhang, W.-W.; Zhang, X.-G.; Li, J.-H. *J. Org. Chem.* **2010**, *75*, 5259−5264. (i) Reddy, P. V.; Srinivas, P.; Annapurna, M.; Bhargava, S.; Wagler, J.; Mirzadeh, N.; Kantam, M. L. *Adv. Synth. Catal.* **2013**, *355*, 705−710. (j) Park, K.; Bae, G.; Moon, J.; Choe, J.; Song, K. H.; Lee, S. *J. Org. Chem.* **2010**, *75*, 6244−6251. (k) Kim, Y.; Park, A.; Park, K.; Lee, S. *Tetrahedron Lett.* **2011**, *52*, 1766−1769. (l) Park, K.; Bae, G.; Park, A.; Kim, Y.; Choe, J.; Song, K. H.; Lee, S. *Tetrahedron Lett.* **2011**, *52*, 576−580. (m) Li, T.-Y.; Sun, P.; Yang, H.-L.; Zhu, Y.; Yan, H.; Lu, L.-H.; Mao, J.-C. *Tetrahedron* **2012**, *68*, 6413−6419. (n) Tartaggia, S.; Lucchi, O. D.; Goossen, L. J. *Eur. J. Org. Chem.* **2012**, 1431−1438.

(5) (a) Ren, G.-R.; Cui, X.-L.; Yang, E.-B.; Yang, F.; Wu, Y.-J. *Tetrahedron* **2010**, *66*, 4022−4028. (b) Huo, S.-Q.; Wu, Y.-J.; Du, C.-X.; Zhu, Y.; Yuan, H.-Z.; Mao, X.-A. *J. Organomet. Chem.* **1994**, *483*, 139−146. (c) Yang, F.; Cui, X.-L.; Li, Y.-N.; Zhang, J.-L.; Ren, G.-R.; Wu, Y.-J. *Tetrahedron* **2007**, *63*, 1963−1969. (d) Yang, F.; Wu, Y.-J. *Eur. J. Org. Chem.* **2007**, 3476−3479. (e) Xu, K.; Hu, H.; Yang, F.; Wu, Y.-J. *Eur. J. Org. Chem.* **2013**, 319−325. (f) Leng, Y.-T.; Yang, F.; Wei, K.; Wu, Y.-J. *Tetrahedron* **2010**, *66*, 1244−1248. (g) Yang, F.; Zhang, J.-L.; Wu, Y.-J. *Tetrahedron* **2011**, *67*, 2969−2973. (h) Xu, K.; Yang, F.; Zhang, G.-D.; Wu, Y.-J. *Green Chem.* **2013**, *15*, 1055−1060.

(6) Wu, M.-Y.; Mao, J.-C.; Guo, J.; Ji, S.-J. *Eur. J. Org. Chem.* **2008**, 4050−4054.

(7) Feng, C.; Loh, T. P. *Chem. Commun.* **2010**, *46*, 4779−4781.

(8) Xie, C.-S.; Liu, L.-F.; Zhang, Y.-H.; Xu, P.-X. *Org. Lett.* **2008**, *10*, 2393−2396.

(9) Tan, L.-M.; Sem, Z.-Y.; Chong, W.-Y.; Liu, X.-Q.; Hendra; Kwan, W.-L.; Lee, C.-L. K. *Org. Lett.* **2013**, *15*, 65−67.

(10) Panda, B.; Sarkar, T. K. *Chem. Commun.* **2010**, *46*, 3131−3133.

(11) Truong, T.; Daugulis, O. *Org. Lett.* **2011**, *13*, 4172−4175.

(12) Mino, T.; Shirae, Y.; Saito, T.; Sakamoto, M.; Fujita, T. *J. Org. Chem.* **2006**, *71*, 9499−9502.

(13) Liang, Y.; Xie, Y.-X.; Li, J.-H. *J. Org. Chem.* **2006**, *71*, 379−381.

(14) Huang, H.; Liu, H.; Jiang, H.; Chen, K. *J. Org. Chem.* **2008**, *73*, 6037−6040.

(15) Finke, A. D.; Elleby, E. C.; Boyd, M. J.; Weissman, H.; Moore, J. S. *J. Org. Chem.* **2009**, *74*, 8897−8900.

(16) Fabrizi, G.; Goggiamani, A.; Sferrazza, A.; Cacchi, S. *Angew. Chem., Int. Ed.* **2010**, *49*, 4067−4070.

(17) Mao, J.-C.; Xie, G.-L.; Wu, M.-Y.; Guo, J.; Ji, S.-J. *Adv. Synth. Catal.* **2008**, *350*, 2477−2482.

(18) Bernini, R.; Cacchi, S.; Fabrizi, G.; Forte, G.; Petrucci, F.; Prastaro, A.; Niembro, S.; Shafir, A.; Vallribera, A. *Org. Biomol. Chem.* **2009**, *7*, 2270−2273.

(19) Wang, S.-H.; Wang, M.; Wang, L.; Wang, B.; Li, P.-H.; Yang, J. *Tetrahedron* **2011**, *67*, 4800−4806.

(20) Pankajakshan, S.; Loh, T. P. *Chem.—Asian J.* **2011**, *6*, 2291−2295.

(21) Shirakawa, E.; Kitabata, T.; Otsuka, H.; Tsuchimoto, T. *Tetrahedron* **2005**, *61*, 9878−9885.

(22) Liu, N.; Liu, C.; Xu, Q.; Jin, Z.-L. *Eur. J. Org. Chem.* **2011**, 4422−4428.

(23) Gilbert, G. C.; Weerasooriya, U. *J. Org. Chem.* **1982**, *47*, 1837−1845.