Research Paper

Journal of Chemical Research

Recyclable and reusable $PdCl_2(PPh_3)_2$/PEG-400/H_2O system for the hydrophenylation of alkynes with sodium tetraphenylborate

Journal of Chemical Research
1–7

DOI: 10.1177/1747519820934379
journals.sagepub.com/home/chl
SAGE

Rong Liu, Tingli Zhang, Bin Huang and Mingzhong Cai

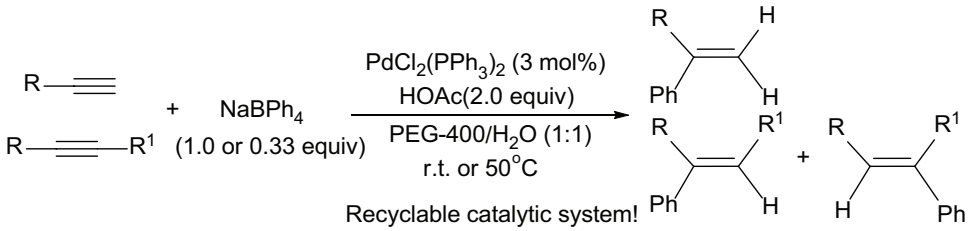
Abstract

A stable and efficient $PdCl_2(PPh_3)_2$/PEG-400/H_2O catalytic system for the hydrophenylation reaction of alkynes has been developed. In the presence of 3 mol% $PdCl_2(PPh_3)_2$ and 2 equiv. of HOAc, the hydrophenylation of both terminal and internal alkynes with sodium tetraphenylborate proceeded smoothly in a mixture of PEG-400 and water at room temperature or 50 °C to afford a variety of phenyl-substituted alkenes in moderate to high yields. The isolation of the products was easily performed by extraction with petroleum ether, and the $PdCl_2(PPh_3)_2$/PEG-400/H_2O system could be readily recycled and reused six times without apparent loss of catalytic activity.

Keywords

alkyne, green chemistry, hydrophenylation, palladium, PEG-400

Date received: 7 April 2020; accepted: 23 May 2020



Introduction

Styrenes are important structural motifs extensively presented in pharmaceuticals, natural or synthetic products, and functional materials.[1–5] Traditionally, styrenes are prepared by the Wittig[6] or Peterson olefinations[7] and insertions of alkynes into organometallic reagents,[8–10] which are waste-intensive and require prefunctionalized starting materials. Catalytic methods such as the olefin metathesis[11,12] and Heck coupling reactions[13] are more atom-economic but also employ prefunctionalized arenes as substrates. In addition, C–H vinylations of the Fujiwara–Moritani type have provided an efficient route to styrenes, but stoichiometric oxidants are required.[14–16]

In recent years, catalytic hydroarylation of alkynes has attracted considerable interest because it allows for the atom-economical construction of functionalized alkenes from relatively simple arenes and alkynes.[17–19] The hydroarylations of alkynes catalyzed by transition metal complex or Lewis acid through C–H bond activation of arenes have been widely investigated, but most research has mainly focused on the electron-rich arenes, and the regiocontrol of the reaction is still difficult, thereby providing a mixture of alkene derivatives.[20–23] Recently, the employment of arylboron compounds in hydroarylation reactions drew considerable attention because of their ready availability, stability, and high functional group compatibility.[24–28] Hayashi et al.[29] reported hydroarylation of alkynes with arylboronic acids, and the reaction has been expanded to the arylative cyclization of aldehydes and alkyne-tethered alkenes.[30,31] Sodium tetraphenylborate is a stable and inexpensive phenylating reagent and has been widely used in organic synthesis. Palladium-catalyzed hydrophenylation of alkenes[32] and alkynes[33] with sodium tetraphenylborate has been reported to proceed smoothly under mild conditions. However, the hydrophenylation

Key Laboratory of Functional Small Organic Molecule, Ministry of Education and Department of Chemistry, Jiangxi Normal University, Nanchang, P.R. China

Corresponding author:
Mingzhong Cai, Key Laboratory of Functional Small Organic Molecule, Ministry of Education and Department of Chemistry, Jiangxi Normal University, Nanchang 330022, P.R. China.
Email: caimzhong@163.com

reaction generally proceeds in the presence of a homogeneous palladium catalyst such as $Pd(OAc)_2$ or $PdCl_2(PPh_3)_2$, which makes the recovery of the expensive palladium catalyst tedious if not impossible and might cause unacceptable palladium contamination of the product. Therefore, from the standpoint of green and sustainable chemistry, the development of recyclable and reusable palladium catalytic systems for these important organic transformations is highly desirable.

As green organic synthesis is attracting more and more attention, the use of eco-friendly, green solvents is highly desirable. To address the recyclability of metal catalysts and environmental concerns, a convenient and efficient way is to anchor the catalyst in a liquid phase by dissolving it into a nonvolatile and nonmixing liquid, such as poly(ethylene glycols) (PEGs)[34–36] and ionic liquids.[37] Generally, ionic liquids require a complicated preparative procedure, and their environmental safety is still being debated because the toxicity and environmental burden data are unknown for most of the ionic liquids. By contrast, PEGs are easily available and cheap, thermally stable, biodegradable, recoverable, and nontoxic liquid polymers which can be used as efficient media for eco-friendly and safe chemical reactions. Recently, PEGs have been widely utilized as green solvents for the palladium-catalyzed carbon–carbon bond-forming reactions such as the Heck coupling,[38] the Suzuki coupling,[39–41] the homo-coupling and cross-coupling of aryl halides,[42] the direct arylation of 1,2,3-triazoles with aryl bromides,[43] the Hiyama coupling,[44] carbonylative Suzuki coupling,[45] carbonylative Sonogashira coupling,[46] and the homo-coupling of arylboronic acids[47] with easy recyclability of the solvents and Pd catalysts. However, to the best of our knowledge, no palladium-catalyzed hydrophenylation reaction of alkenes or alkynes with sodium tetraphenylborate in PEGs has been described until now. Herein, we report the application of $PdCl_2(PPh_3)_2$/PEG-400/H_2O system as a highly efficient and reusable catalytic medium for the hydrophenylation of alkynes with sodium tetraphenylborate. This affords a variety of phenyl-substituted alkenes in moderate to high yields. The developed methodology shows important practical advantages deserving special note.

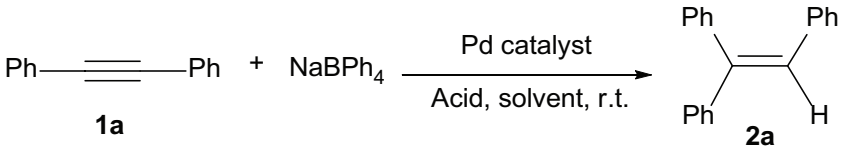
Results and discussion

In our initial screening experiments, the hydrophenylation of 1,2-diphenylacetylene (**1a**) with $NaBPh_4$ was selected as model reaction to optimize the reaction conditions. The effects of acids, solvents, and palladium catalysts on the reaction were studied, and the results are given in Table 1. At first, the acid effect was examined using $PdCl_2(PPh_3)_2$ (1 mol%) as catalyst with PEG-400 as solvent at room temperature (entries 1–3). It is evident that the reaction produced only a trace of target product **2a** in the absence of any acid additive (Table 1, entry 1), and a low yield of **2a** was obtained when 1 equiv. of HCl was used as the additive (Table 1, entry 2). However, when 1 equiv. of HOAc was used as the additive, the reaction was improved and afforded the desired **2a** in 38% yield (Table 1, entry 3). Increasing the amount of HOAc or palladium catalyst loading was found to further promote the reaction, and moderate yields were achieved (Table 1, entries 4–6). Our next studies focused on the influence of solvent on the model reaction. It was found that a mixture of PEG-400 and water was more effective than PEG-400 alone as solvent (Table 1, entries 7–10). The reaction performed in PEG-400/H_2O (*V/V*, 1:1) gave the desired **2a** in 94% yield (Table 1, entry 9). In addition, the efficiency of various chain length PEGs on the model reaction was investigated (Table 1, entries 11 and 12). PEG-400 was found to be superior to PEG-600 and PEG-1000. Other palladium catalysts such as $Pd(OAc)_2$, $PdCl_2$, and $Pd(PPh_3)_4$ were also tested, but none of them exhibited good catalytic activity (Table 1, entries 13–15). Reducing palladium loading from 3 to 1 mol% resulted in a significant decrease in the yield of **2a** (Table 1, entry 16). Thus, the optimal catalytic system involved the use of $PdCl_2(PPh_3)_2$ (3 mol%), HOAc (2.0 equiv.) in PEG-400/H_2O (*V/V*, 1:1) at room temperature under Ar for 6 h (Table 1, entry 9).

Having achieved satisfactory results in the hydrophenylation of 1,2-diphenylacetylene with $NaBPh_4$, then, various internal and terminal alkynes were examined to explore the scope of substrates under the optimized reaction conditions and the results are listed in Table 2. As expected, symmetrical internal alkynes **1b–d** displayed a similar reactivity as **1a** and the hydrophenylation reactions proceeded smoothly to give the corresponding trisubstituted phenyl alkenes **2b–d** in 70%–84% yields. Furthermore, the hydrophenylation of electron-poor internal alkyne **1e** provided the adduct **2e** in 80% yield. As for unsymmetrical internal alkynes, the reactions also took place effectively, and the regioselectivity depends on the nature of substituents. For example, the use of methyl but-2-ynoate **1f** or ethyl but-2-ynoate **1g** led to the formation of methyl 3-phenyl-2-butenoate **2f** or ethyl 3-phenyl-2-butenoate **2g**, respectively, in excellent yields and regioselectivity, indicating that the phenyl group was almost exclusively added to the β-carbon of the ynoate due to the presence of the strongly polarized C–C triple bond. The reaction of ethyl oct-2-ynoate **1h** also proceeded smoothly with high yield, but a slightly lower regioselectivity of 93% was observed. Notably, ethyl 3-phenylpropiolate **1i** showed a similar reactivity as **1f** and **1g** to furnish the expected product **2i** in 92% yield and excellent regioselectivity. But, in the case of 1-phenylpropyne **1j**, the two regioisomers **2j** and **3j** resulted from the *cis*-addition of $NaBPh_4$ to **1j** were obtained in 43% and 32% yields, respectively. To our delight, when terminal alkynes were used as substrates, the hydrophenylation reactions also worked well with high regioselectivity in favor of the Markovnikov adducts. For instance, the hydrophenylation reactions of 1-hexyne **1k**, 1-octyne **1l**, and 5-phenyl-1-pentyne **1n** afforded the corresponding phenyl-substituted alkenes **2k**, **2l**, and **2n**, respectively, in 78%–89% yields. However, in the cases of phenylacetylene **1m**, 5-chloro-1-pentyne **1o**, and 5-cyano-1-pentyne **1p**, the corresponding adducts **2m**, **2o**, and **2p** were obtained in relatively lower yields of 48%–60%.

Sodium tetraarylborates are usually prepared by the reaction of arylmagnesium bromides with trimethyl

Table 1. Reaction of 1,2-diphenylacetylene (**1a**) with $NaBPh_4$.[a]



1a **2a**

Entry	Pd catalyst (mol%)	Solvent (*V*/*V*)	Acid (equiv. to **1a**)	Yield (%)[b]
1	$PdCl_2(PPh_3)_2$ (1)	PEG-400	None	Trace
2	$PdCl_2(PPh_3)_2$ (1)	PEG-400	HCl (1.0)	9
3	$PdCl_2(PPh_3)_2$ (1)	PEG-400	HOAc (1.0)	38
4	$PdCl_2(PPh_3)_2$ (1)	PEG-400	HOAc (2.0)	48
5	$PdCl_2(PPh_3)_2$ (2)	PEG-400	HOAc (2.0)	58
6	$PdCl_2(PPh_3)_2$ (3)	PEG-400	HOAc (2.0)	67
7	$PdCl_2(PPh_3)_2$ (3)	PEG-400/H_2O (3:1)	HOAc (2.0)	78
8	$PdCl_2(PPh_3)_2$ (3)	PEG-400/H_2O (2:1)	HOAc (2.0)	86
9	$PdCl_2(PPh_3)_2$ (3)	PEG-400/H_2O (1:1)	HOAc (2.0)	94
10	$PdCl_2(PPh_3)_2$ (3)	PEG-400/H_2O (1:2)	HOAc (2.0)	91
11	$PdCl_2(PPh_3)_2$ (3)	PEG-600/H_2O (1:1)	HOAc (2.0)	87
12	$PdCl_2(PPh_3)_2$ (3)	PEG-1000/H_2O (1:1)	HOAc (2.0)	74
13	$Pd(OAc)_2$ (3)	PEG-400/H_2O (1:1)	HOAc (2.0)	11
14	$PdCl_2$ (3)	PEG-400/H_2O (1:1)	HOAc (2.0)	15
15	$Pd(PPh_3)_4$ (3)	PEG-400/H_2O (1:1)	HOAc (2.0)	29
16	$PdCl_2(PPh_3)_2$ (1)	PEG-400/H_2O (1:1)	HOAc (2.0)	48

[a]Reactions were carried out with **1a** (1.0 mmol), $NaBPh_4$ (1.0 mmol), palladium catalyst, and acid in solvent (2 mL) in a sealed tube at room temperature under Ar for 6 h.
[b]Isolated yield.

borate, followed by hydrolysis. To explore the scope of the borates, we prepared sodium tetrakis(4-methylphenyl) borate via a complicated procedure starting from 4-bromotoluene, magnesium turnings, and trimethyl borate. The reaction of ethyl but-2-ynoate **1g** with sodium tetrakis(4-methylphenyl)borate also proceeded smoothly under the conditions presented in Table 2 to afford the desired (*E*)-ethyl 3-*p*-tolylbut-2-enoate **4b** in 88% yield with regioselectivity of 99%.

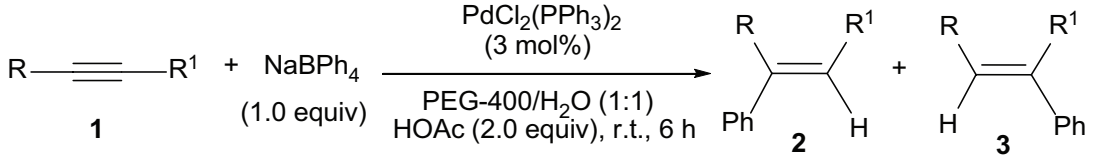
To explore the possibility for further efficient transfer of phenyl groups in $NaBPh_4$, we examined the reaction of **1a** with 0.33 equiv. of $NaBPh_4$ in PEG-400/H_2O (1:1) under different conditions. It was found that when the reaction was carried out at 50 °C for 12 h, the desired product **2a** was produced in 91% yield, indicating that at most three phenyl groups in $NaBPh_4$ could be efficiently utilized. We next performed the reaction of 0.33 equiv. of $NaBPh_4$ with several other alkynes at 50 °C in PEG-400/H_2O (1:1), and the results are given in Table 3. As shown in Table 3, both symmetrical and unsymmetrical internal alkynes underwent the hydrophenylation reaction smoothly to afford the corresponding adducts in good to high yields. But, the reactions of terminal alkynes **1l–n** with 0.33 equiv. of $NaBPh_4$ gave the desired products **2l–n** in only 39%–54% yields.

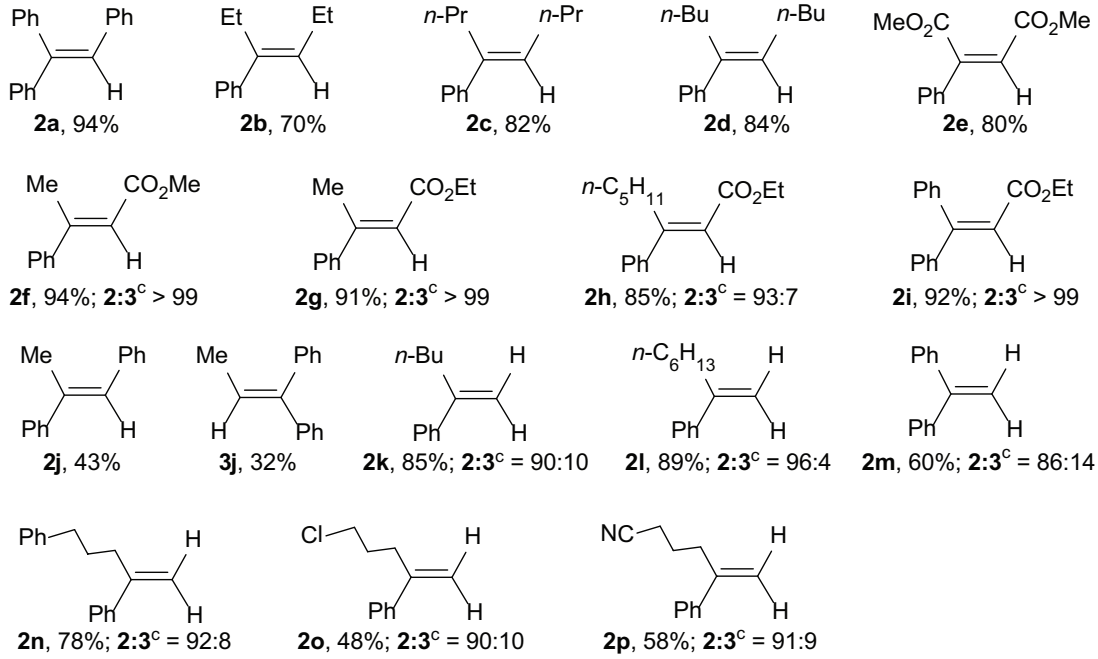
It was reported that the reaction of $NaBPh_4$ with HOAc could produce Ph_3B, benzene, and NaOAc, and Ph_3B could react with H_2O further to form di- and monophenylboronic acid.[32] Thus, we also studied the reactivity of arylboronic acids with alkynes at room temperature (Scheme 1). As shown in Scheme 1, the palladium-catalyzed hydroarylation reaction of internal alkynes with various arylboronic acids also took place smoothly at room temperature in PEG-400/H_2O (1:1) to give the corresponding trisubstituted aryl alkenes in moderate yields. We next carried out the reaction of 1,2-diphenylacetylene **1a** with $PhB(OH)_2$ under the conditions shown in Scheme 1 for direct comparison to the sodium tetraphenylborate, but the desired **2a** was isolated in only 55% yield.

A possible mechanism for the palladium-catalyzed hydrophenylation of alkynes with $NaBPh_4$ is illustrated in Scheme 2. First, oxidative addition of the C–B bond of Ph_3B formed in situ from reaction of $NaBPh_4$ with HOAc to $(Ph_3P)_2Pd(0)$ produces intermediate **A**.[32] Subsequent selective insertion of the alkyne **1** into the Pd–C bond gives intermediate **B**, which undergoes a hydrolysis reaction to provide intermediate **C**. Finally, reductive elimination of intermediate **C** affords the desired phenyl-substituted alkene **2** and regenerates $(Ph_3P)_2Pd(0)$ to complete the catalytic cycle. In addition to Ph_3B, Ph_2BOH and $PhB(OH)_2$ could also be possible intermediates in the palladium-catalyzed hydrophenylation reaction of alkynes with $NaBPh_4$.

To evaluate the reusability of the solvent and the catalyst, the hydrophenylation reaction of 1,2-diphenylacetylene (1 mmol) with $NaBPh_4$ (1 mmol) was investigated in the presence of $PdCl_2(PPh_3)_2$ (3 mol%) and HOAc (2.0 equiv.) in PEG-400/H_2O (*V*/*V* = 1:1, 2 mL) at room temperature. As shown in Table 4, we were pleased to observe that the $PdCl_2(PPh_3)_2$/PEG-400/H_2O system could be recycled and reused up to six times without apparent loss of catalytic activity. After initial experimentation, the reaction mixture was extracted with petroleum ether (3 × 10 mL), and the

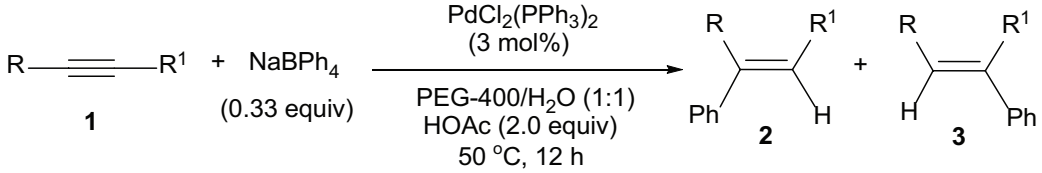
Table 2. $PdCl_2(PPh_3)_2$-catalyzed hydrophenylation reaction of alkynes with $NaBPh_4$ in PEG-400/H_2O.[a,b]

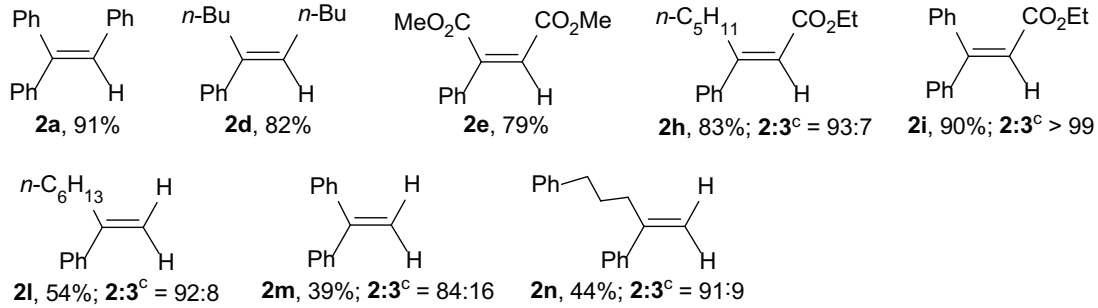




[a]Reactions were carried out with alkyne (1.0 mmol), $NaBPh_4$ (1.0 mmol), HOAc (2.0 mmol), and $PdCl_2(PPh_3)_2$ (0.03 mmol) in a mixture of PEG-400 (1 mL) and H_2O (1 mL) in a sealed tube at room temperature under Ar for 6 h.
[b]Isolated yield.
[c]Determined by GC.

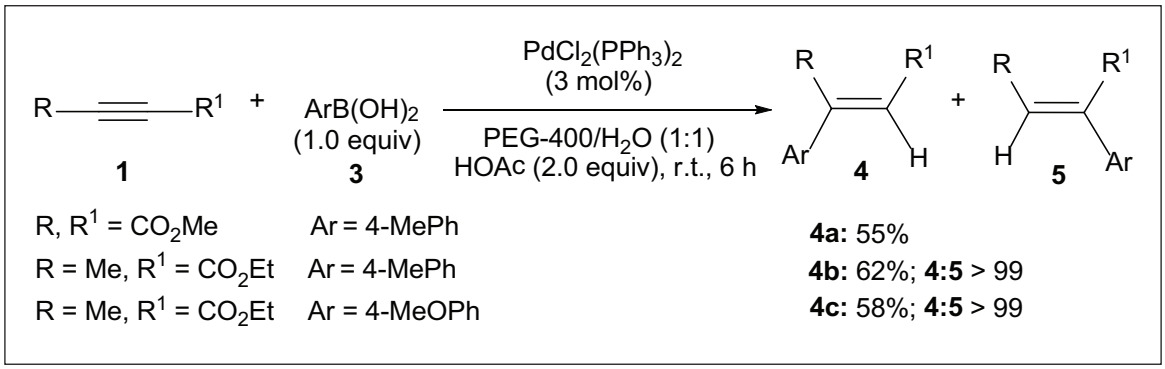
Table 3. Palladium-catalyzed hydrophenylation of alkynes with $NaBPh_4$ (0.33 equiv.) in PEG-400/H_2O.[a,b]



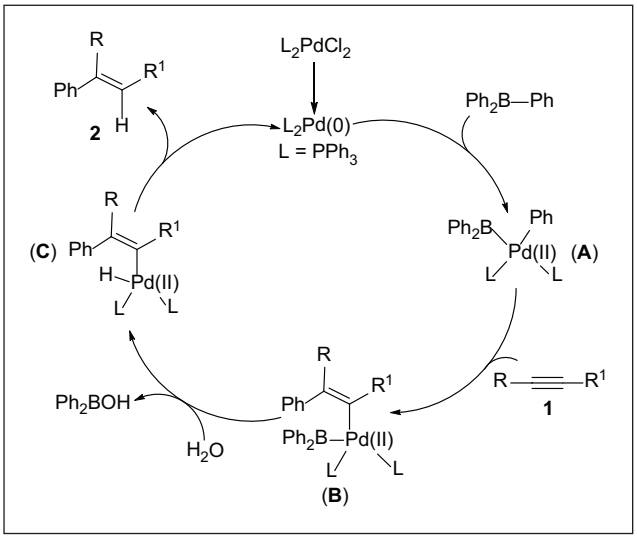


[a]Reactions were carried out with alkyne (1.0 mmol), $NaBPh_4$ (0.33 mmol), HOAc (2.0 mmol), and $PdCl_2(PPh_3)_2$ (0.03 mmol) in a mixture of PEG-400 (1 mL) and H_2O (1 mL) in a sealed tube at 50 °C under Ar for 12 h.
[b]Isolated yield.
[c]Determined by GC.

$PdCl_2(PPh_3)_2$/PEG-400/H_2O system was then subjected to a second run of the reaction by charging with the same starting materials (1,2-diphenylacetylene, $NaBPh_4$, and HOAc) without addition of $PdCl_2(PPh_3)_2$. In addition, the leaching of palladium in the product was also determined, and inductively coupled plasma (ICP) analysis of the crude petroleum



Scheme 1. Palladium-catalyzed hydroarylation reaction of alkynes with arylboronic acids in PEG-400/H_2O (1:1).



Scheme 2. Proposed catalytic cycle.

ether extract after the first cycle showed that palladium content was less than 0.80 ppm.

In conclusion, an efficient and recyclable catalytic system for the palladium-catalyzed hydrophenylation reaction of alkynes with sodium tetraphenylborate has been developed. In the presence of 3 mol% $PdCl_2(PPh_3)_2$ and HOAc, the hydrophenylation reaction of a variety of alkynes with $NaBPh_4$ proceeded smoothly at room temperature in PEG-400/H_2O (1:1) to afford the corresponding phenyl-substituted alkenes in moderate to high yields. Furthermore, the $PdCl_2(PPh_3)_2$/PEG-400/H_2O system could be recycled up to six times without apparent loss of catalytic activity. The present protocol will serve as an efficient and green way to prepare a variety of phenyl-substituted alkenes. Currently, further efforts to extend the application of the system in other palladium-catalyzed organic transformations are underway in our laboratory.

Experimental

All reagents were purchased from different commercial sources and used as received without further purification unless otherwise indicated. All reactions were carried out under Ar in a sealed reaction tube with magnetic stirring and the solvents needed to be de-gassed. ^{1}H NMR spectra were recorded on a Bruker Avance 400 (400 MHz) spectrometer with tetramethylsilane (TMS) as an internal standard using $CDCl_3$ as the solvent. ^{13}C NMR spectra were recorded on a Bruker Avance 400 (100 MHz) spectrometer using $CDCl_3$ as the solvent. HRMS spectra were recorded on a quadrupole–time of flight Bruker MicroTOF-Q II mass spectrometer equipped with an electrospray ionization (ESI) and atmospheric pressure chemical ionization (APCI) source. Palladium content was determined with inductively coupled plasma atom emission Atomscan16 (ICP-AES, TJA Corporation).

General procedure for palladium-catalyzed hydrophenylation of alkynes with $NaBPh_4$ in PEG-400/H_2O (1:1)

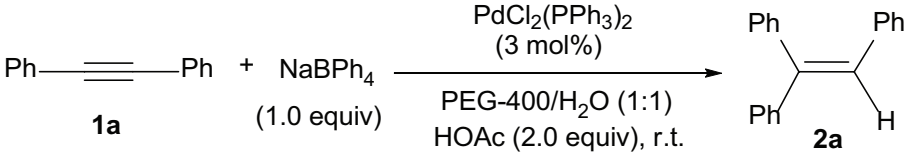
A mixture of alkyne **1** (1.0 mmol), $NaBPh_4$ (1.0 mmol), HOAc (2.0 mmol), $PdCl_2(PPh_3)_2$ (0.03 mmol), PEG-400 (1.0 mL), and H_2O (1.0 mL) was stirred under Ar in a sealed tube at room temperature for 6 h. After completion of the reaction, the reaction mixture was extracted three times with petroleum ether (3 × 10 mL). The combined ether phase was concentrated under reduced pressure, and the residue was purified by flash column chromatography on silica gel (eluting with petroleum ether) to afford the desired product **2**.

The residue (the aqueous layer) of the extraction was heated to 60 °C in vacuum for 20 min to remove the residual petroleum ether, and then subjected to a second run of the reaction by charging with the same starting materials (alkyne, $NaBPh_4$, and HOAc) without addition of $PdCl_2(PPh_3)_2$ under identical conditions. After the first reaction cycle, the crude petroleum ether extract was subjected to ICP-AES analysis before any further purification.

1,1,2-Triphenylethene (**2a**): Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36-6.90 (m, 16H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.5, 142.7, 140.4, 137.5, 130.5, 129.6, 128.7, 128.3, 128.2, 127.7, 127.5, 127.4, 126.8, 126.6.[33]

(E)-3-phenylhex-3-ene (**2b**): Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37-7.16 (m, 5H), 5.64 (t, J = 7.2 Hz, 1H), 2.51 (q, J = 7.4 Hz, 2H), 2.22-2.18 (m, 2H), 1.06 (t, J = 7.4 Hz, 3H), 0.99 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.2, 141.1, 130.1, 128.2, 126.5, 126.3, 22.8, 21.8, 14.4, 13.8.[33]

Table 4. Recyclability of $PdCl_2(PPh_3)_2$/PEG-400/H_2O system.[a]



Cycle	Time (h)	Yield (%)[b]	Cycle	Time (h)	Yield (%)[b]
1	6	94	4	6	93
2	6	93	5	7	92
3	6	94	6	8	91

[a]Reaction conditions: **1a** (1 mmol), $NaBPh_4$ (1 mmol), $PdCl_2(PPh_3)_2$ (3 mol%), HOAc (2 mmol), and PEG-400/H_2O (1:1, 2.0 mL) at room temperature under Ar.
[b]Isolated yield.

(E)-4-phenyloct-4-ene (**2c**): Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36-7.18 (m, 5H), 5.66 (t, *J* = 7.2 Hz, 1H), 2.48 (t, *J* = 7.6 Hz, 2H), 2.19-2.15 (m, 2H), 1.49-1.44 (m, 2H), 1.38-1.33 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H), 0.88 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.7, 140.1, 129.3, 128.2, 126.4, 31.8, 30.8, 23.2, 21.9, 14.1.[33]

(E)-5-phenyldec-5-ene (**2d**): Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34-7.18 (m, 5H), 5.64 (t, *J* = 7.2 Hz, 1H), 2.49 (t, *J* = 6.8 Hz, 2H), 2.22-2.18 (m, 2H), 1.43-1.26 (m, 8H), 0.93 (t, *J* = 7.0 Hz, 3H), 0.87 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.6, 140.1, 129.1, 128.1, 126.3, 114.8, 32.1, 31.0, 29.5, 28.3, 22.7, 22.5, 14.1, 14.0.[33]

(Z)-dimethyl 2-phenylmaleate (**2e**): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51-7.37 (m, 5H), 6.31 (s, 1H), 3.94 (s, 3H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.3, 165.4, 149.0, 133.2, 130.6, 129.0, 126.8, 117.1, 52.7, 52.0.[33]

(E)-methyl 3-phenylbut-2-enoate (**2f**): Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49-7.34 (m, 5H), 6.14 (q, *J* = 1.4 Hz, 1H), 3.76 (s, 3H), 2.59 (d, *J* = 1.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.4, 155.9, 142.2, 129.1, 128.6, 126.3, 116.8, 51.2, 18.1.[33]

(E)-ethyl 3-phenylbut-2-enoate (**2g**): Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48-7.26 (m, 5H), 6.13 (s, 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 2.57 (s, 3H), 1.31 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.8, 155.4, 142.3, 128.9, 128.5, 126.3, 117.3, 59.8, 17.9, 14.3. HRMS calcd for $C_{12}H_{14}O_2^+$ [M^+]: 190.0994; found: 190.0988.

(E)-ethyl 3-phenyloct-2-enoate (**2h**): Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45-7.32 (m, 5H), 6.01 (s, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 3.09 (t, *J* = 7.6 Hz, 2H), 1.45-1.26 (m, 9H), 0.85 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.5, 160.8, 141.6, 128.7, 128.5, 126.7, 117.3, 59.8, 31.9, 31.0, 28.7, 22.4, 14.3, 14.0.[33]

Ethyl 3,3-diphenylacrylate (**2i**): Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42-7.21 (m, 10H), 6.39 (s, 1H), 4.08 (q, *J* = 7.2 Hz, 2H), 1.13 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.1, 156.5, 140.8, 129.4, 129.1, 128.5, 128.4, 128.3, 127.9, 117.5, 60.1, 14.0.[33]

(E)-1,2-diphenylpropene (**2j**): White solid; m.p. 81–82 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53 (d, *J* = 7.2 Hz, 2H), 7.39-7.22 (m, 8H), 6.84 (s, 1H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.2, 138.5, 137.7, 129.3, 128.6, 128.3, 127.7, 127.3, 126.7, 126.2, 17.6.[33]

1,1-Diphenylpropene (**3j**): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39-7.16 (m, 10H), 6.17 (q, *J* = 7.2 Hz, 1H), 1.75 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.1, 142.7, 140.2, 130.3, 128.3, 128.2, 127.4, 127.1, 126.8, 124.4, 15.8.[33]

2-Phenyl-1-hexene (**2k**): Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46-7.28 (m, 5H), 5.30 (s, 1H), 5.09 (d, *J* = 1.2 Hz, 1H), 2.54 (t, *J* = 7.4 Hz, 2H), 1.50-1.36 (m, 4H), 0.94 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.9, 141.6, 128.2, 127.2, 126.1, 112.0, 35.1, 30.5, 22.4, 13.9.[48]

2-Phenyl-1-octene (**2l**): Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40-7.23 (m, 5H), 5.25 (s, 1H), 5.04 (s, 1H), 2.49 (t, *J* = 7.2 Hz, 2H), 1.46-1.27 (m, 8H), 0.85 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.8, 141.6, 128.2, 127.2, 126.1, 112.0, 35.4, 31.7, 29.0, 28.3, 22.6, 14.1.[33]

1,1-Diphenylethene (**2m**): Brown oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34-7.23 (m, 10H), 5.46 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.2, 141.6, 128.3, 128.2, 127.7, 114.2.[33]

2,5-Diphenyl-1-pentene (**2n**): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38-7.13 (m, 10H), 5.28 (s, 1H), 5.07 (s, 1H), 2.64 (t, *J* = 7.0 Hz, 2H), 2.54 (t, *J* = 7.2 Hz, 2H), 1.79-1.74 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.4, 142.3, 141.4, 128.5, 128.3, 127.3, 126.2, 125.7, 112.4, 35.5, 34.9, 29.9. HRMS calcd for $C_{17}H_{18}^+$ [M^+]: 222.1409; found: 222.1414.

5-Chloro-2-phenyl-1-pentene (**2o**): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43-7.25 (m, 5H), 5.33 (d, *J* = 1.4 Hz, 1H), 5.11 (d, *J* = 1.4 Hz, 1H), 3.54 (t, *J* = 6.4 Hz, 2H), 2.68 (t, *J* = 7.4 Hz, 2H), 1.96-1.87 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.9, 140.7, 128.4, 127.5, 126.1, 113.3, 44.4, 32.4, 31.0.[48]

5-Cyano-2-phenyl-1-pentene (**2p**): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42-7.28 (m, 5H), 5.38 (s, 1H), 5.16 (s, 1H), 2.72 (t, *J* = 7.2 Hz, 2H), 2.35 (t, *J* = 7.2 Hz, 2H), 1.86-1.79 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.2, 140.2, 128.5, 127.8, 126.1, 119.4, 114.0, 34.0, 23.8, 16.4. HRMS calcd for $C_{12}H_{13}N^+$ [M^+]: 171.1048; found: 171.1046.

General procedure for palladium-catalyzed hydroarylation of alkynes with $ArB(OH)_2$ in PEG-400/H_2O (1:1)

A mixture of alkyne **1** (1.0 mmol), $ArB(OH)_2$ **3** (1.0 mmol), HOAc (2.0 mmol), $PdCl_2(PPh_3)_2$ (0.03 mmol), PEG-400 (1.0 mL), and H_2O (1.0 mL) was stirred under Ar in a sealed tube at room temperature for 6 h. After the reaction, the mixture was extracted three times with petroleum ether (3 × 10 mL). The combined ether phase was concentrated under reduced pressure, and the residue was purified by flash column chromatography on silica gel (eluting with petroleum ether) to afford the target product **4**.

(Z)-dimethyl 2-p-tolylmaleate (**4a**): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 6.31 (s, 1H), 3.97 (s, 3H), 3.80 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.5, 165.6, 149.0, 141.2, 130.4, 129.8, 126.7, 115.9, 52.7, 52.0, 21.4. HRMS calcd for $C_{13}H_{14}O_4^+$ [M^+]: 234.0892; found: 234.0887.

(E)-ethyl 3-p-tolylbut-2-enoate (**4b**): Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 7.6 Hz, 2H), 6.13 (s, 1H), 4.20 (q, *J* = 7.2 Hz, 2H), 2.56 (s, 3H), 2.36 (s, 3H), 1.31 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.6, 153.9, 139.1, 137.7, 128.4, 126.4, 118.2, 51.9, 21.3, 18.2, 14.4. HRMS calcd for $C_{13}H_{16}O_2^+$ [M^+]: 204.1150; found: 204.1152.

(E)-ethyl 3-(4-methoxyphenyl)but-2-enoate (**4c**): Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45 (d, *J* = 8.8 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.11 (s, 1H), 4.20 (q, *J* = 6.8 Hz, 2H), 3.83 (s, 3H), 2.56 (s, 3H), 1.31 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.1, 160.4, 154.9, 134.4, 127.7, 115.4, 113.9, 59.7, 55.4, 17.7, 14.4. HRMS calcd for $C_{13}H_{16}O_3^+$ [M^+]: 220.1099; found: 220.1096.

Declaration of conflicting interests

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

Funding

The author(s) disclosed receipt of the following financial support for the research, authorship, and/or publication of this article: This study was financially supported by the National Natural Science Foundation of China (no. 21462021) and the Natural Science Foundation of Jiangxi Province of China (no. 20161BAB203086).

ORCID iD

Mingzhong Cai https://orcid.org/0000-0002-1056-2846

References

1. Rosazza JPN, Huang Z, Dostal L, et al. *J Ind Microbiol* 1995; 15: 457.
2. Ali MS, Mahmud S, Perveen S, et al. *Phytochemistry* 1999; 50: 1385.
3. Rukachaisirikul V, Rodglin A, Sukpondma Y, et al. *J Nat Prod* 2012; 75: 853.
4. Hassam M, Taher A, Arnott GE, et al. *Chem Rev* 2015; 115: 5462.
5. Roseblade SJ and Pfaltz A. *Acc Chem Res* 2007; 40: 1402.
6. March J. *Advanced organic chemistry: reactions, mechanism, and structure*. 4th ed. New York: Wiley, 1992.
7. Kurti L and Czako B. *Strategic applications of named reactions in organic synthesis: background and detailed mechanisms*. Amsterdam: Elsevier Academic Press, 2005.
8. Xu X, Chen J, Gao W, et al. *Tetrahedron* 2010; 66: 2433.
9. Fagnou K and Lautens M. *Chem Rev* 2003; 103: 169.
10. Shirakawa E, Yamagami T, Kimura T, et al. *J Am Chem Soc* 2005; 127: 17164.
11. Grubbs RH and Chang S. *Tetrahedron* 1998; 54: 4413.
12. Fürstner A. *Angew Chem Int Ed* 2000; 39: 3012.
13. Beletskaya IP and Cheprakov AV. *Chem Rev* 2000; 100: 3009.
14. Moritani I and Fujiwara Y. *Tetrahedron Lett* 1967; 8: 1119.
15. Yokota T, Tani M, Sakaguchi S, et al. *J Am Chem Soc* 2003; 125: 1476.
16. Nishikata T and Lipshutz BH. *Org Lett* 2010; 12: 1972.
17. Kakiuchi F and Murai S. *Acc Chem Res* 2002; 35: 826.
18. Nevado C and Echavarren AM. *Synthesis* 2005: 167.
19. Kitamura T. *Eur J Org Chem* 2009: 1111.
20. Jia C, Piao D, Oyamada J, et al. *Science* 2000; 287: 1992.
21. Tsukada N, Mitsuboshi T, Setoguchi H, et al. *J Am Chem Soc* 2003; 125: 12102.
22. Yamaguchi M, Kido Y, Hayashi A, et al. *Angew Chem Int Ed* 1997; 36: 1313.
23. Reetz MT and Sommer K. *Eur J Org Chem* 2003: 3485.
24. Sakai M, Hayashi H and Miyaura N. *Organometallics* 1997; 16: 4229.
25. Takaya Y, Ogasawara M and Hayashi T. *J Am Chem Soc* 1998; 120: 5579.
26. Hayashi T, Senda T, Takaya Y, et al. *J Am Chem Soc* 1999; 121: 11591.
27. Hayashi T, Ueyama K, Tokunaga N, et al. *J Am Chem Soc* 2003; 125: 11508.
28. Chen F-X, Kina A and Hayashi T. *Org Lett* 2006; 8: 341.
29. Hayashi T, Inoue K, Taniguchi N, et al. *J Am Chem Soc* 2001; 123: 9918.
30. Shintani R, Okamoto K, Otomaru Y, et al. *J Am Chem Soc* 2004; 126: 54.
31. Shintani R, Tsurusaki A, Okamoto K, et al. *Angew Chem Int Ed* 2005; 44: 3909.
32. Cho CS, Motofusa S-I, Ohe K, et al. *J Org Chem* 1995; 60: 883.
33. Zeng H and Hua R. *J Org Chem* 2008; 73: 558.
34. Chen J, Spear SK, Huddleston JG, et al. *Green Chem* 2005; 7: 64.
35. Candeias NR, Branco LC, Gois PMP, et al. *Chem Rev* 2009; 109: 2703.
36. Turgis R, Billault I, Acherar S, et al. *Green Chem* 2013; 15: 1016.
37. Hallett JP and Welton T. *Chem Rev* 2011; 111: 3508.
38. Chandrasekhar S, Narsihmulu C, Sultana SS, et al. *Org Lett* 2002; 4: 4399.
39. Li J-H, Liu W-J and Xie Y-X. *J Org Chem* 2005; 70: 5409.
40. Liu L, Zhang Y and Wang Y. *J Org Chem* 2005; 70: 6122.
41. Han W, Liu C and Jin Z-L. *Org Lett* 2007; 9: 4005.
42. Wang L, Zhang Y, Liu L, et al. *J Org Chem* 2006; 71: 1284.
43. Ackermann L and Vicente R. *Org Lett* 2009; 11: 4922.
44. Shi S and Zhang Y. *J Org Chem* 2007; 72: 5927.
45. Zhou Q, Wei S and Han W. *J Org Chem* 2014; 79: 1454.
46. Zhao H, Cheng M, Zhang J, et al. *Green Chem* 2014; 16: 2515.
47. Xia J, Cheng M, Chen Q, et al. *Appl Organometal Chem* 2015; 29: 113.
48. Pasto DJ, Garves K and Sevenair JP. *J Org Chem* 1968; 33: 2975.