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Recyclable and reusable PdCl₂(PPh₃)₂/PEG-2000/ H₂O system for the carbonylative Sonogashira coupling reaction of aryl iodides with alkynes†

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 $PdCl_2(PPh_3)_2$ in a mixture of water and poly(ethylene glycol) (PEG-2000) is shown to be an extremely active catalyst for the carbonylative Sonogashira coupling reaction of aryl iodides with terminal alkynes. The reaction can be conducted under an atmospheric pressure of carbon monoxide at 25 °C with Et₃N as a base, yielding a variety of alkynyl ketones in good to excellent yields. Application of this synthetic method to prepare flavones from *o*-iodophenol and terminal alkynes was also achieved. The isolation of the products is readily achieved by extraction with diethyl ether, and the PdCl₂(PPh₃)₂/PEG-2000/H₂O system can be easily recycled and reused six times without any loss of catalytic activity.

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Introduction

The synthesis of alkynyl ketones has attracted considerable interest because of their appearance in many biologically active molecules and because they are key intermediates in the synthesis of natural products and drug-like molecules.¹⁻⁵ Traditionally, alkynyl ketones are generally prepared via the direct coupling reaction of acid chlorides with alkynyl organometallic reagents such as silver,⁶ copper,⁷ sodium,⁸ lithium,⁹ cadmium,¹⁰ zinc,¹¹ silicon,¹² and tin.¹³ However, these methods require the use of dry solvents under an inert atmosphere. An alternative synthetic procedure for alkynyl ketones is the palladium-catalyzed coupling of acyl chlorides with terminal alkynes in the presence of CuI.14-18 The transition-metal-catalyzed coupling reaction of alkynes or their metalated derivatives, such as alkynylstannanes19,20 and alkynylsilanes,²¹ with organic halides in the presence of CO provides a convenient route to alkynyl ketones under atmospheric conditions with atom economy. Kang et al. reported that iodonium salts can readily undergo carbonylative coupling with terminal alkynes in the presence of Pd(OAc)₂/CuI catalysts and an atmospheric pressure of carbon monoxide in DME-H₂O (4:1) medium at room temperature, affording the desired alkynyl ketones in good yields.22 Mori and Mohamed Ahmed

reported that the palladium-catalyzed carbonylative Sonogashira coupling of terminal alkynes with aryl iodides under an atmospheric pressure of carbon monoxide could be accomplished by using aqueous ammonia as a base in THF at room temperature with or without CuI.23 Recently, Yang and co-workers reported that the palladium-catalyzed copper-free carbonylative Sonogashira coupling of terminal alkynes with aryl iodides under an atmospheric pressure of carbon monoxide could be achieved by using water as a solvent at room temperature with 3 equiv. of Et₃N as a base.²⁴ The carbonylative Sonogashira coupling reaction generally proceeds in the presence of a homogeneous palladium catalyst such as Pd(OAc)₂, PdCl₂(PPh₃)₂, and PdCl₂.²²⁻²⁴ However, industrial applications of these homogeneous palladium catalysts remain a challenge because they are expensive and cannot be recycled. Therefore, from the standpoint of green chemistry, the development of a recyclable and reusable catalyst system that allows for the highly efficient carbonylative Sonogashira coupling of a wide range of substrates (aryl iodides and terminal alkynes) is worthwhile.

As environmentally friendly "green" syntheses are becoming more and more important, it is desirable to avoid the use of any hazardous and expensive organic solvents. There are also significant economical and environmental reasons for developing recyclable catalytic reactions from both academic and industrial perspectives. To satisfy both recyclability and environmental concerns, a more facile method is to immobilize the catalyst in a liquid phase by dissolving it in a nonvolatile and nonmixing liquid, such as ionic liquids^{25–29} and PEG.^{30–36} Although ionic liquids offer some advantages, the tedious preparation of ionic liquids and their environmental safety is still debated since data on their toxicity and

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environmental burden are for the most part unknown. However, poly(ethylene glycols) (PEGs), possessing negligible vapor pressure, are known to be inexpensive, thermally stable, recoverable, nontoxic compounds which serve as suitable media for environmentally friendly and safe chemical reactions.³⁷⁻⁴² So far, PEGs have been successfully used as reaction media for palladium-catalyzed carbon-carbon coupling reactions, such as the Heck reaction,³⁰ the Suzuki-Miyaura reaction,^{31,32} the homocoupling and cross-coupling of aryl halides,³³ and the direct arylation of 1,2,3-triazoles with aryl bromides³⁴ with easy recyclability of the solvent and palladium catalysts. Recently, Wang and co-workers reported a Pd-(PPh₃)₄-PEG 400 catalyzed protocol for the atom-efficient Stille cross-coupling reactions of organotins with aryl bromides.43,44 We herein report the application of a PdCl₂(PPh₃)₂/PEG-2000/ H₂O system as an extremely effective and reusable catalytic medium for the carbonylative Sonogashira coupling reaction of aryl iodides with terminal alkynes under an atmospheric pressure of carbon monoxide.

Results and discussion

The effect of PEG on the carbonylative Sonogashira coupling reaction of aryl iodides with terminal alkynes in water was initially investigated. The carbonylative coupling of 4-iodoanisole (2 mmol) and phenylacetylene (2.4 mmol) with CO was chosen as the model reaction. The reaction was carried out in water (3 g) in the presence of 5 mol% of PdCl₂(PPh₃)₂ using Et₃N (4 mmol) as base at 25 °C for 24 h under an atmospheric pressure of carbon monoxide. In the absence of PEG-2000, the result was not promising, and a low yield was obtained (Fig. 1). The yield of 1-(4-methoxyphenyl)-3-phenylpropynone increased with the addition of incremental PEG-2000 and an excellent yield was obtained when the amount of PEG-2000 reached 3 g. Further increasing the amount of PEG-2000 resulted in a decrease in yield. It was noteworthy that only a trace amount of the desired product was formed using neat PEG-2000 as the solvent at 50 °C (Table 1, entry 1). On the



Fig. 1 Effect of PEG-2000 on the carbonylative coupling reaction of 4-iodoanisole with phenylacetylene in water.

other hand, the phosphine-free $PdCl_2$ - or $Pd(OAc)_2$ -catalyzed carbonylative coupling reaction in PEG-2000/H₂O medium was also tested; however, a palladium precipitate was formed very rapidly under the reductive reaction conditions (CO, H₂O).

To compare the effect of PEG in different organic solvents, the carbonylative Sonogashira coupling reaction was performed under identical conditions in mixtures of PEG-2000 and various organic solvents, including THF, dioxane, CH₂Cl₂, toluene, acetonitrile and MeOH (Table 1). The combination of PEG-2000 with nonpolar toluene and aprotic polar solvents, such as THF, dioxane, CH2Cl2, acetonitrile, and MeOH, afforded the desired product in low yields (Table 1, entries 2-7). On the other hand, the mixture of PEG-2000 with water furnished the coupling product in excellent yield (Table 1, entry 8). These results show a significant solvent effect on the reaction, and that water is a good solvent for the carbonylative Sonogashira coupling reaction in the presence of PEG. Our next studies focused on the effect of various bases on the model reaction in PEG-2000/H2O medium. When 2 equiv. of ammonia (0.5 M) was used as a base,²³ the reaction did not occur and the starting materials were recovered completely (Table 1, entry 9). Bu₃N also afforded a good yield (Table 1, entry 10), while other bases such as pyridine, DBU, TMEDA, and DABCO gave moderate yields (Table 1, entries 11-14). The use of Na₂CO₃, K₂CO₃, Cs₂CO₃, K₃PO₄ and NaOAc delivered the product in very low yields (Table 1, entries 15-19). So, Et₃N was the best choice for the model reaction in PEG-2000/H₂O medium (Table 1, entry 8). In addition, the efficiency of various chain length PEGs on the reaction was also examined under the same reaction conditions (Table 1, entries 20-22). PEG-2000 was superior to PEG-600, PEG-1000 and PEG-4000.

As a result of these studies, we were encouraged to examine the reaction with a broad range of substrates to determine the specificity and scope of substrates for this system. Thus, a variety of aryl iodides were reacted with phenylacetylene, and the results are listed in Table 2. As shown in Table 2, it is evident that most of the carbonylative coupling reactions proceeded smoothly under mild conditions in the PEG-2000/H2O medium, affording good to excellent yields of the coupling products and that many functional groups were tolerated in these reactions. Generally, the aryl iodides with electron-donating groups, such as methoxy and methyl, gave excellent yields (Table 2, entries 1–5). Even the reaction of sterically hindered 2-iodoanisole with phenylacetylene gave the desired coupling product 3c in 94% yield (Table 2, entry 3). The presence of a strong electron-withdrawing group, such as -NO2, -COMe and -CO₂Me, on the aryl iodide is known to promote the direct coupling, producing noncarbonylative coupling products. As discussed in Mori and Mohamed Ahmed's research,²³ a mixture of carbonylative and noncarbonylative coupling products were obtained when electron-deficient aryl iodides were used as substrates in the carbonylative coupling reaction, presumably because the alkyne reacts too rapidly with the arylpalladium(II) intermediate derived from the rapid oxidative addition of electron-deficient aryl iodide to palladium(0) complex without insertion of CO. However, the reaction of

Paper

Table 1 Carbonylative coupling reaction of 4-iodoanisole with phenylacetylene in various media^a

	$MeO - (1 + CO (1 atm) + = Ph \xrightarrow{5 \text{ mol% } PdCl_2(PPh_3)_2} FMeO - Ph$				
Entry	Base	Solvent ^b	Yield ^c (%)		
1^d	Et ₃ N	PEG-2000	13		
2	Et_3N	PEG-2000-THF	18		
3	Et_3N	PEG-2000-dioxane	20		
4	Et_3N	PEG-2000-CH ₂ Cl ₂	35		
5	Et_3N	PEG-2000-toluene	38		
6	Et_3N	PEG-2000–MeCN	46		
7	Et_3N	PEG-2000–MeOH	55		
8	Et_3N	PEG-2000-H ₂ O	93		
9	$NH_3 (0.5 M)$	PEG-2000-H ₂ O	0		
10	Bu ₃ N	PEG-2000-H ₂ O	86		
11	Pyridine	PEG-2000-H ₂ O	67		
12	DBU	PEG-2000-H ₂ O	60		
13	TMEDA	PEG-2000-H ₂ O	63		
14	DABCO	PEG-2000-H ₂ O	59		
15	Na_2CO_3	PEG-2000-H ₂ O	23		
16	K_2CO_3	PEG-2000-H ₂ O	25		
17	Cs_2CO_3	PEG-2000-H ₂ O	31		
18	K_3PO_4	PEG-2000-H ₂ O	17		
19	NaOAc	PEG-2000-H ₂ O	11		
20	Et_3N	PEG-600-H ₂ O	67		
21	Et_3N	PEG-1000-H ₂ O	83		
22	$\mathrm{Et}_3\mathbf{N}$	PEG-4000-H ₂ O	78		

^{*a*} Reaction conditions: 4-iodoanisole (2 mmol), phenylacetylene (2.4 mmol), CO (1 atm), base (4 mmol). ^{*b*} The amount of water or solvent was 3 mL, PEG was 3 g. ^{*c*} Isolated yields. ^{*d*} At 50 °C.

1-chloro-4-iodobenzene having an electron-withdrawing substituent afforded the desired coupling product 3h in 82% yield, along with only 10% yield of 4-chlorodiphenylacetylene under optimized conditions (Table 2, entry 8), the same reaction in the presence of 5 mol% of PdCl₂(dppf) in THF using aq. NH₃ (0.5 M) as base at room temperature for 12 h gave 3h in 67% vield.²³ The reaction of methyl 4-iodobenzoate provided a 57% yield of the carbonylative coupling product 3i and a 32% yield of 4-methoxycarbonyldiphenylacetylene (Table 2. entry 9), but the reaction of 4-nitroiodobenzene with a strong electron-withdrawing substituent only gave a trace of desired coupling product, and 4-nitrodiphenylacetylene was formed in 87% yield. Interestingly, the unprotected 2-aminoiodobenzene can participate in the reaction, and the desired product was obtained in good yield (Table 2, entry 7). In addition, the reactions of bulky 1-iodonaphthalene and heteroaryl iodides such as 2-iodothiophene also proceeded smoothly to give the corresponding coupling products 3j and 3k in good yields. This new catalyst system towards the carbonylative Sonogashira coupling reaction of aryl iodides is more efficient than the published PdCl₂(PPh₃)₂/THF/aq. NH₃ system.²³ The high efficiency of the PdCl₂(PPh₃)₂/PEG-2000/H₂O system is probably attributed to the properties of PEG as the cosolvent^{45,46} and PTC.

To further evaluate the reaction, we next examined the carbonylative coupling reaction of alkyl-substituted terminal alkynes and substituted phenylacetylenes with methyl- and methoxy-substituted aryl iodides, and the results are summarized in Table 3. Mori and Mohamed Ahmed reported that the

carbonylative coupling reaction of terminal alkynes bearing an alkyl substituent with aryl iodides was slow and required the use of CuI as a cocatalyst, where moderate to good yields were obtained.²³ It is noteworthy that the coupling reaction of aryl iodides with terminal alkynes bearing alkyl substituents catalyzed by our catalytic system was achieved by performing the reaction without CuI as a cocatalyst. A plausible mechanism is shown in Scheme 1. First $PdCl_2(PPh_3)_2$ is reduced to Pd(0) $(PPh_3)_2$ by CO and H_2O .^{23,24} The oxidative addition of an aryl iodide to $Pd(0)(PPh_3)_2$ provides arylpalladium(II) complex (A), which is followed by migratory insertion of carbon monoxide giving acylpalladium(II) complex (B). Subsequent transmetalation between B and a terminal alkyne in the presence of a base and reductive elimination of alkynyl ketone (D) from the intermediate (C) regenerates $Pd(0)(PPh_3)_2$. We reasoned that in the absence of CuI, the less reactive terminal alkyne (compared with its corresponding alkynyl copper ate complex) would easily react with the electron-deficient acylpalladium(II) complex (B) rather than its precursor arylpalladium(II) complex (A); therefore, the desired carbonylative coupling reaction could be secured. The formation of palladium black was not observed during the carbonylative coupling reaction due to the presence of the phosphine ligand. The TEM measurement showed that there is no palladium nanoparticle present in the reaction. So, the real catalytic species should be $Pd(0)(PPh_3)_2$ in the PEG-2000/H2O phase.

The results listed in Table 3 show that the carbonylative coupling reactions of a variety of aliphatic alkynes, such as 1-octyne, 1-hexyne, 3,3-dimethyl-1-butyne, cyclopropylacetylene

 Table 2
 Carbonylative coupling of various aryl iodides with phenylacetylene^a

Entry	Aryl iodide	Alkyne	Product	Yield ^{b} (%)
1	MeO			93
2	MeO			91
3	OMe	=-		94
4	Me	$\equiv -\langle \rangle$		91
5	Me			90
6				86
7		=-		83
8	СН			82
9				57
10				81
11	ζ _s ,			69

^{*a*} Reaction conditions: aryl iodide (2 mmol), phenylacetylene (2.4 mmol), Et₃N (4 mmol), CO (1 atm), water (3 g), PEG-2000 (3 g) at 25 °C for 24 h. ^{*b*} Isolated yields.

and 3-methoxypropyne, with various aryl iodides proceeded smoothly under mild conditions to afford the corresponding carbonylative coupling products **3l–3w** in good to excellent yields (Table 3, entries **1–12**). The reactions of even the sterically hindered 2-iodoanisole with various aliphatic alkynes also gave good to excellent yields (Table 3, entries 2, 6, 9 and 11). The reaction of trimethylsilylacetylene with 4-methyliodobenzene afforded the corresponding alkynyl ketone **3x** in 82% yield (Table 3, entry 13). The reactions of the substituted phenylacetylenes, such as 4-methylphenylacetylene with 4-iodoanisole and 2-iodoanisole, also proceeded effectively under the same conditions to yield 90 and 86% of the desired coupling products **3y** and **3z**, respectively (Table 3, entries 14 and 15). The results above prompted us to investigate the reaction of aryl bromides, but the carbonylative coupling reaction did not occur under the conditions optimized for the iodides. Aryl chlorides were also not reactive and the reaction of 4-chloroiodobenzene with phenylacetylene could afford selectively 1-(4-chlorophenyl)-3-phenylpropynone (**3h**) in 82% yield (Table 2, entry 8).

Flavones are an important class of naturally occurring products,^{47–49} and many methods for their preparations have been published.^{50–58} Recently, the palladium-catalyzed carbonylation of *o*-iodophenol derivatives with terminal alkynes to prepare flavones has attracted considerable interest.^{59–65} We also investigated the feasibility of preparing flavones by the sequential carbonylative coupling of *o*-iodophenol with terminal alkynes to form α , β -unsaturated ketones, followed by an intramolecular cyclization to give flavones in a one-pot operation using PdCl₂(PPh₃)₂/PEG-2000/H₂O as

Table 3 Carbonylative coupling of various alkynes with aryl iodides^a

Ar-L + CO (1 atm) + = \mathbf{R} $\frac{5 \text{ mol% PdCl}_2(\text{PPh}_3)_2, \text{ Et}_3\text{N} (2 \text{ equiv})}{\text{Ar} - \mathbf{C}}$						
	1	2 PEG-2000 (3 g), H	2 PEG-2000 (3 g), H ₂ O (3 g), 25 °C, 24 h 3			
Entry	Aryl iodide	Alkyne	Product	$\operatorname{Yield}^{b}(\%)$		
1	MeO-	<u></u> —C ₆ H ₁₃ - <i>n</i>	MeO-C-C-C ₆ H ₁₃ - <i>n</i>	91		
2		<u></u> —C ₆ H ₁₃ - <i>n</i>	$ \begin{array}{c} \begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \end{array} \end{array} \\ \begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \\ \end{array} \\ \begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \\ \\ \end{array} \\ \begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \\ \end{array} \\ \begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \\ \end{array} \\ \begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \end{array} \\ \begin{array}{c} \\ \\ \\ \\ \\ \\ \end{array} \\ \begin{array}{c} \\ \\ \\ \\ \\ \\ \end{array} \\ \begin{array}{c} \\ \\ \\ \\ \\ \\ \end{array} \\ \begin{array}{c} \\ \\ \\ \\ \\ \\ \end{array} \\ \begin{array}{c} \\ \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \\ \end{array} \\ \begin{array}{c} \\ \\ \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \\ \end{array} \\ \end{array} \\ \\ \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \\ \end{array} $	87		
3	Me	<u></u> —−C ₆ H ₁₃ - <i>n</i>	$Me - C_{6}H_{13}-n$	88		
4		<u></u> —−C ₆ H ₁₃ - <i>n</i>	$ \begin{array}{c} & & \\ & & $	90		
5	MeO-	<u></u> —C₄H ₉ - <i>n</i>	Me ² 30 MeO-CC4H ₉ - <i>n</i>	85		
6		<u></u> —−C ₄ H ₉ - <i>n</i>	3p	88		
7		<u></u> —C₄H ₉ - <i>n</i>	O_{OMe} $3q$	82		
8	MeO-	──C₄H ₉ -t	$MeO - C_4H_9 - t$	91		
9		───C₄H ₉ - <i>t</i>	$ \begin{array}{c} & & \\ & & $	95		
10	MeO-	$\equiv \checkmark$		87		
11		$\equiv \triangleleft$		81		
12	Me	───CH ₂ OMe		86		
13	Me	───SiMe ₃	Me-C-SiMe ₃	82		
14	MeO			90		
15		——————————————————————————————————————	Me Me Me	86		

^{*a*} Reaction conditions: aryl iodide (2 mmol), alkyne (2.4 mmol), Et₃N (4 mmol), CO (1 atm), water (3 g), PEG-2000 (3 g) at 25 °C for 24 h. ^{*b*} Isolated yields.

catalyst system (Scheme 2). The results show that the tandem carbonylative coupling/intramolecular cyclization reaction of various terminal alkynes such as 1-hexyne, 3,3-dimethyl-1-

butyne and trimethylsilylacetylene with *o*-iodophenol could proceed smoothly to afford the desired flavones **4a–4c** in moderate to good yields.



Scheme 1 Possible explanation for the carbonylative coupling reactions.



Scheme 2 Synthesis of flavones.

To check the reusability of PEG-2000 and the catalyst, the carbonylative coupling reaction of 4-iodoanisole with phenylacetylene was examined in the presence of 5 mol% $PdCl_2(PPh_3)_2$. After initial experimentation, the reaction mixture was extracted with diethyl ether (4×15 mL), and the solidified PdCl₂(PPh₃)₂/PEG-2000/H₂O was subjected to a second run by charging with the same substrates (4-iodoanisole, phenylacetylene, and Et₃N) under 1 atm of CO without any regeneration or addition of PdCl₂(PPh₃)₂. We were gratified to observe that the PdCl₂(PPh₃)₂/PEG-2000/H₂O system could be recycled and reused six times without any loss of activity. The results of six runs showed that they were almost consistent in yields and rates (93%, 91%, 94%, 92%, 93%, and 92%, respectively, for 24 h). In addition, the leaching of palladium in the product was also determined. ICP analysis of the extract found that palladium content was less than 0.65 ppm.

Conclusions

In summary, a highly efficient and reusable $PdCl_2(PPh_3)_2/PEG-2000/H_2O$ system for the carbonylative Sonogashira coupling reaction has been developed. In the presence of $PdCl_2(PPh_3)_2$, the carbonylative coupling reactions of a number of terminal alkynes, including alkyl- and aryl-substituted acetylenes, with various aryl iodides under an atmospheric pressure of carbon monoxide proceeded smoothly and efficiently at 25 °C using Et₃N as base in a mixture of PEG-2000 and water to afford the desired alkynyl ketones in

good to excellent yields. Application of this synthetic method to generate flavones from *o*-iodophenol and terminal alkynes was also achieved. Furthermore, the $PdCl_2(PPh_3)_2/PEG-2000/H_2O$ system could be recycled and reused six times without any loss of catalytic activity. This protocol will serve as an efficient and green way to prepare alkynyl ketones and 2-substituted flavones. Currently, further efforts to extend the application of the system in other palladium-catalyzed transformations are underway in our laboratory.

Experimental

All chemicals were of reagent grade and used as purchased. All solvents were dried and distilled before use. The products were purified by flash chromatography on silica gel. A mixture of EtOAc and hexane was generally used as eluent. All carbonylative coupling products were characterized by comparison of their spectra and physical data with authentic samples. IR spectra were determined on a Perkin-Elmer 683 instrument. ¹H NMR spectra were recorded on a Bruker Avance 400 (400 MHz) spectrometer with TMS as an internal standard in CDCl₃ as solvent. ¹³C NMR spectra were recorded on a Bruker Avance 400 (100 MHz) spectrometer in CDCl₃ as solvent. Melting points are uncorrected.

General procedure for the carbonylative Sonogashira coupling in $PEG-2000/H_2O$

A 50 mL round-bottomed flask equipped with a gas inlet tube and a magnetic stirring bar was charged with PEG-2000 (3 g), water (3 g), PdCl₂(PPh₃)₂ (0.1 mmol), and Et₃N (4 mmol). The mixture was heated to 50 °C with stirring. The flask was flushed with carbon monoxide, and the mixture was slowly cooled to 25 °C and then aryl iodide (2 mmol) and alkyne (2.4 mmol) were added. After being stirred at 25 °C for 24 h under CO (1 atm), the resulting suspension was extracted four times with diethyl ether $(4 \times 15 \text{ mL})$. The residue of the extraction was subjected to a second run of the carbonylative coupling reaction by charging with the same substrates (aryl iodide, terminal alkyne, and Et₃N) under the same conditions without further addition of PdCl₂(PPh₃)₂ or PEG. The combined ether phase was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexane–ethyl acetate = 20:1).

General procedure for the synthesis of flavones

A 50 mL round-bottomed flask equipped with a gas inlet tube and a magnetic stirring bar was charged with PEG-2000 (3 g), water (3 g), $PdCl_2(PPh_3)_2$ (0.1 mmol), and Et_3N (4 mmol). The mixture was heated to 50 °C with stirring. The flask was flushed with carbon monoxide, and the mixture was slowly cooled to 25 °C and then *o*-iodophenol (2 mmol) and alkyne (2.4 mmol) were added. After being stirred at 25 °C for 48 h under CO (1 atm), the resulting suspension was extracted four times with diethyl ether (4 × 15 mL). The combined ether phase was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexane-ethyl acetate = 8:1).

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