Recyclable and reusable \( \text{PdCl}_2(\text{PPh}_3)_2/\text{PEG-400}/\text{H}_2\text{O} \) system for the hydrophenylation of alkynes with sodium tetraphenylborate

Rong Liu, Tingli Zhang, Bin Huang and Mingzhong Cai

Abstract
A stable and efficient \( \text{PdCl}_2(\text{PPh}_3)_2/\text{PEG-400}/\text{H}_2\text{O} \) catalytic system for the hydrophenylation reaction of alkynes has been developed. In the presence of 3 mol\% \( \text{PdCl}_2(\text{PPh}_3)_2 \) 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 \( \text{PdCl}_2(\text{PPh}_3)_2/\text{PEG-400}/\text{H}_2\text{O} \) system could be readily recycled and reused six times without apparent loss of catalytic activity.

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

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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 vinylation of the Fujiwara–Moritani type have provided an efficient route to styrenes, but stoichiometric oxidants are required.\(^14\)\(^-\)\(^16\)

In recent years, catalytic hydroyloration 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 hydroyloration 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 hydroyloration reactions drew considerable attention because of their ready availability, stability, and high functional group compatibility.\(^24\)\(^-\)\(^28\) Hayashi et al.\(^29\) reported hydroyloration of alkynes with arylboronic acids, and the reaction has been expanded to the arylative cyclization of aldehydes and alkynetethered alkenes.\(^30\)\(^,\)\(^31\) Sodium tetraphenylborate is a stable and inexpensive phenylating reagent and has been widely used in organic synthesis. Palladium-catalyzed hydroyloration of alkenes\(^32\) and alkynes\(^33\) with sodium tetraphenylborate has been reported to proceed smoothly under mild conditions. However, the hydroyloration reaction generally proceeds in the presence of a homogenous palladium catalyst such as \( \text{Pd(OAc)}_2 \) or \( \text{PdCl}_2(\text{PPh}_3)_2 \), 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 in a nonvolatile and nonmixing liquid, such as poly(ethylene glycols) (PEGs)\(^34\)\(^-\)\(^36\) and ionic liquids.\(^37\)

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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 homocoupling and cross-coupling of aryl halides,\(^{42}\) the direct arylation of 1,2,3-triazoles with aryl bromides,\(^{43}\) the Hiyama coupling,\(^{44}\) carboxylative Suzuki coupling,\(^{45}\) carboxylative Sonogashira coupling,\(^{46}\) and the homo-coupling of arylboronic acids 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\(_2\)O (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\(_3\))\(_2\) 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\(_2\)O (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 alkenes 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 alkenes 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 alkenes, the reactions also took place effectively, and the regioselectivity depends on the nature of substituents. For example, the use of methyl but-2-yne 1f or ethyl but-2-yne 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-yne 1h also proceeded smoothly with high yield, but a slightly lower regioselectivity of 93% was observed. Notably, ethyl 3-phenylpropionate 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 alkenes 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 1-pentynyl-1-pentyne 1m afforded the corresponding phenyl-substituted alkkenes 2k, 2l, and 2m, respectively, in 78%–89% yields. However, in the cases of phenylacetylene 1n, 5-chloro-1-pentyne 1o, and 5-cyano-1-pentyne 1p, the corresponding adducts 2n, 2o, and 2p were obtained in relatively lower yields of 48%–60%.

Sodium tetraarylborates are usually prepared by the reaction of aryllithium bromides with trimethyl borate, followed by hydrolysis. To explore the scope of the borates, we prepared sodium tetras-(4-methylphenyl)borate via a complicated procedure starting from 4-bromotoluene, magnesium turnings, and trimethyl borate. The reaction of ethyl but-2-ynone 1g with sodium tetras-(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\(_2\)O (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 alkenes at 50°C in PEG-400/H\(_2\)O (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\(_3\)B, benzene, and NaOAc, and Ph\(_3\)B could react with H\(_2\)O 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\(_2\)O (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\(_3\)B formed in situ from reaction of NaBPh\(_4\) with HOAc to \((\text{Ph}_3\text{P})_2\text{Pd}(0)\) 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 \((\text{Ph}_3\text{P})_2\text{Pd}(0)\) to complete the catalytic cycle. In addition to Ph\(_3\)B, Ph\(_2\)BOH and PhBr(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), palladium catalyst, and acid in solvent (2 mL) in a sealed tube at room temperature under Ar for 6 h.

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% \(\text{PdCl}_2(\text{PPh}_3)_2\) and HOAc, the hydrophenylation reaction of a variety of alkynes with NaBPh\(_4\) proceeded smoothly at room temperature in PEG-400/H\(_2\)O (1:1) to afford the corresponding phenyl-substituted alkenes in moderate to high yields. Furthermore, the \(\text{PdCl}_2(\text{PPh}_3)_2\)/PEG-400/H\(_2\)O 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.

### Table 1. Reaction of 1,2-diphenylacetylene (1a) with NaBPh\(_4\)

| Entry | Pd catalyst (mol%) | Solvent (V/V) | Acid (equiv. to 1a) | Yield (%)\(^{a}\) |
|-------|--------------------|---------------|------------------|-----------------|
| 1     | \(\text{PdCl}_2(\text{PPh}_3)_2\) (1) | PEG-400       | None             | Trace           |
| 2     | \(\text{PdCl}_2(\text{PPh}_3)_2\) (1) | PEG-400       | HCl (1.0)        | 9               |
| 3     | \(\text{PdCl}_2(\text{PPh}_3)_2\) (1) | PEG-400       | HOAc (1.0)       | 38              |
| 4     | \(\text{PdCl}_2(\text{PPh}_3)_2\) (2) | PEG-400       | HOAc (2.0)       | 48              |
| 5     | \(\text{PdCl}_2(\text{PPh}_3)_2\) (3) | PEG-400       | HOAc (2.0)       | 58              |
| 6     | \(\text{PdCl}_2(\text{PPh}_3)_2\) (3) | PEG-400/H\(_2\)O (3:1) | HOAc (2.0) | 67 |
| 7     | \(\text{PdCl}_2(\text{PPh}_3)_2\) (3) | PEG-400/H\(_2\)O (2:1) | HOAc (2.0) | 78 |
| 8     | \(\text{PdCl}_2(\text{PPh}_3)_2\) (3) | PEG-400/H\(_2\)O (1:1) | HOAc (2.0) | 86 |
| 9     | \(\text{PdCl}_2(\text{PPh}_3)_2\) (3) | PEG-400/H\(_2\)O (1:2) | HOAc (2.0) | 94 |
| 10    | \(\text{PdCl}_2(\text{PPh}_3)_2\) (3) | PEG-600/H\(_2\)O (1:1) | HOAc (2.0) | 91 |
| 11    | \(\text{PdCl}_2(\text{PPh}_3)_2\) (3) | PEG-1000/H\(_2\)O (1:1) | HOAc (2.0) | 74 |
| 12    | \(\text{PdCl}_2(\text{PPh}_3)_2\) (3) | PEG-1000/H\(_2\)O (1:1) | HOAc (2.0) | 11 |
| 13    | \(\text{PdCl}_2(\text{PPh}_3)_2\) (3) | PEG-1000/H\(_2\)O (1:1) | HOAc (2.0) | 15 |
| 14    | \(\text{PdCl}_2(\text{PPh}_3)_2\) (3) | PEG-1000/H\(_2\)O (1:1) | HOAc (2.0) | 29 |
| 15    | \(\text{PdCl}_2(\text{PPh}_3)_2\) (3) | PEG-1000/H\(_2\)O (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.
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)
A mixture of alkyne 1 (1.0 mmol), NaBPh₄ (1.0 mmol), HOAc (2.0 mmol), PdCl₂(PPh₃)₂ (0.03 mmol), PEG-400 (1.0 mL), and H₂O (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, NaBPh₄, and HOAc) without addition of PdCl₂(PPh₃)₂ under identical conditions. After the first reaction cycle, the crude petroleum ether extract was subjected to ICP-AES analysis before any further purification.

(E)-3-phenylhex-3-ene (2b): Pale yellow oil. ¹H NMR (400 MHz, CDCl₃): 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); ¹³C NMR (100 MHz, CDCl₃): δ = 143.2, 141.1, 130.1, 130.1, 128.2, 126.3, 126.2, 22.8, 21.8, 14.4, 13.8.

(E)-4-phenylpent-4-ene (2c): Pale yellow oil. ¹H NMR (400 MHz, CDCl₃): 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); ¹³C NMR (100 MHz, CDCl₃): δ = 143.6, 140.1, 129.3, 128.2, 126.4, 31.8, 30.8, 23.2, 21.9, 14.1.

(Z)-dimethyl 2-phenylmaleate (2e): Yellow oil. ¹H NMR (400 MHz, CDCl₃): δ = 7.51-7.37 (m, 5H), 6.31 (s, 1H), 3.94 (s, 3H), 3.78 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 168.3, 165.4, 149.0, 133.2, 130.6, 129.0, 126.8, 117.1, 52.7, 52.0.

(E)-methyl 3-phenylbut-2-enoate (2f): Pale yellow oil. ¹H NMR (400 MHz, CDCl₃): 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); ¹³C NMR (100 MHz, CDCl₃): δ = 167.4, 155.9, 142.2, 129.1, 128.6, 126.3, 116.8, 51.2, 18.1.

(E)-ethyl 3-phenylbut-2-enoate (2g): Pale yellow oil. ¹H NMR (400 MHz, CDCl₃): 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).
Table 4. Recyclability of PdCl$_2$(PPh$_3$)$_2$/PEG-400/H$_2$O 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$_2$O (1:1, 2.0 mL) at room temperature under Ar.

$^b$Isolated yield.

3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 166.8, 155.4, 142.3, 128.9, 128.5, 126.3, 117.3, 59.8, 17.9, 14.3. HRMS calced for C$_{12}$H$_{13}$N$_2$; found: 190.0984.

5-Chloro-2-phenyl-1-pentene

3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 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 calced for C$_{12}$H$_{18}$; found: 222.1409; 222.1414.

5-Chloro-2-phenyl-1-pentene

3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 146.2, 146.0, 128.5, 127.8, 126.1, 119.4, 114.0, 34.0, 23.8, 16.4. HRMS calced for C$_{12}$H$_{18}$; found: 171.1048; 171.1046.

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

A mixture of alkyne (1.0 mmol), ArB(OH)$_2$ (1.0 mmol), HOAc (2.0 mmol), PdCl$_2$(PPh$_3$)$_2$ (0.03 mmol), PEG-400 (1.0 mL), and H$_2$O (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-tolylmalate (4a): Yellow oil. 1H NMR (400 MHz, CDCl$_3$): $\delta$ = 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$_3$): $\delta$ = 165.2, 165.6, 149.0, 141.2, 130.4, 129.8, 126.7, 115.9, 52.7, 52.0, 21.4. HRMS calced for C$_{12}$H$_{18}$O$_2$; found: 234.0892; 234.0887.

(E)-ethyl 3-phenyloct-2-enoate (2k): Pale yellow oil. 1H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.40-7.37 (m, 3H), 2.46-2.37 (m, 2H), 1.25-1.16 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 150.2, 146.1, 130.4, 129.8, 126.7, 115.9, 35.4, 31.7, 29.0, 28.3, 22.6, 14.1. 33

1,1-Diphenylethene (2m): Brown oil. 1H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.34-7.23 (m, 10H), 5.46 (s, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 150.2, 146.1, 130.4, 129.8, 126.7, 115.9, 35.4, 31.7, 29.0, 28.3, 22.6, 14.1. 33

1,1-Diphenylethene (2m): Brown oil. 1H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.34-7.23 (m, 10H), 5.46 (s, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 150.2, 146.1, 130.4, 129.8, 126.7, 115.9, 35.4, 31.7, 29.0, 28.3, 22.6, 14.1. 33

2,5-Diphenyl-1-pentene (2n): Yellow oil. 1H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.38-7.17 (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$_3$): $\delta$ = 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 calced for C$_{12}$H$_{18}$; found: 222.1409; 222.1414.
12.64, 118.2, 51.9, 21.3, 18.2, 14.4. HRMS calcd for C_{13}H_{16}O_{3}^{+} [M^+]: 220.1150; found: 220.1152.

(E)-ethyl 3-(4-methoxyphenyl)but-2-enoate (4c): Pale yellow oil. ¹H NMR (400 MHz, CDCl₃): 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); ¹³C NMR (100 MHz, CDCl₃): 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.

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