Palladium-catalyzed phosphine-, copper-free and aerobic Sonogashira coupling in aqueous media

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Abstract

A simple, highly efficient and phosphine-free protocol for the Sonogashira coupling of aryl iodides with terminal alkynes has been developed using $Pd_2(dba)_3$ (dba=dibenzylideneacetone) as the catalyst under aqueous, copper-free and aerobic conditions. The coupling of aryl iodides with aromatic terminal alkynes provided good to excellent yields and moderate to good yields were achieved using aliphatic terminal alkynes as one of the coupling partners. Aqueous ethanol as solvent is economical and environmentally benign in accordance with the concept of green chemistry.

Keywords: Palladium, phosphine-free, aerobic, Sonogashira coupling, aqueous

Introduction

The Sonogashira cross-coupling reaction has become one of the most important methods in the formation of carbon-carbon bonds over the past three decades, which plays an important role in the synthesis of pharmaceuticals, agrochemicals and functional materials.[1] Generally, this reaction proceeds in the presence of phosphine ligands with the combination of palladium and copper salts using a large excess of amine as base or solvent.[1a, 2] However, the copper salts as the co-catalysts would induce homocoupling reaction of terminal alkynes.[3] Moreover, phosphine ligands are also sensitive to air or moisture, which restricts this reaction to proceed only under an inert atmosphere. To solve these problems, efforts have been made including the employment of sole palladium salts as the catalysts (copper-free systems),[4] reducing atmosphere (H_2)[5] (phosphine ligands were still used) and palladium complexes[6] containing air-stable ligands such as *N*-heterocyclic carbene ligands.[7] Although these palladium complexes of air-stable ligands-involved protocols delivered the corresponding products successfully, most of the ligands or palladium complexes prepared *via* multi-synthesis were expensive. Noticeably, among recent advances on this topic, phosphine-free protocols[8] have obtained attention because of its

simplicity and economy in comparison with the ligand-promoted ones, such as $Pd(OAc)_2$ in DMF,[8a] $PdCl_2$ in H_2O,[8b] $Pd(OAc)_2$ in aqueous acetone,[8d] Pd/C in aqueous isopropanol.[8f]

With the enhancement of people's awareness of environment, water-involved Sonogashira reaction has mushroomed.[6f,g,8b-d,8f,9] In comparison with organic solvent, water is an ideal alternative for organic synthesis due to its non-toxic, incombustibility as well as inexpensiveness, which is of great interest to chemists. Very recently, we reported a palladium-catalyzed phosphine-free protocol for the Suzuki reaction in aqueous ethanol.[10] To the best of our knowledge, the palladium-catalyzed phosphine-free Sonogashira reaction in aqueous ethanol has not been reported. In the present paper, we intend to develop an aerobic and water-involved phosphine-free system for the palladium-catalyzed Sonogashira reaction under mild and copper-free conditions.

Results and Discussion

Investigation of reaction conditions

Initially the coupling of 4-iodoanisole and phenylacetylene was chosen as the model reaction for screening the reaction conditions. The corresponding results are collected in Table 1. Firstly, the effects of solvents on this Sonogashira reaction were investigated. Obviously, the coupling in water with ethanol as the co-solvent provided the highest isolated yield than those with other organic solvents under the same amount of water (Table 1, entry 4). The coupling in aqueous glycol was hardly to obtain the desired product (Table 1, entry 2). Only a 26% yield was obtained with respect to DMF as the co-solvent (Table 1, entry 1).

It was noteworthy that the amount of water had a marked effect on the coupling of the 4-iodoanisole with phenylacetylene (Table 1, entries 4-8). Only a 44% yield was obtained when the reaction proceeded in pure ethanol (Table 1, entry 5). Increasing the water content to 25%, the coupling gave 91% yield (Table 1, entry 6). With further increasing the water content to 60%, the yield was decreased to 28% (Table 1, entry 7). When the water content accounted for three fourths of solvent, the yield was sharply decreased to trace (Table 1, entry 8). Therefore, the suitable volume ratio of ethanol to water is 3:1.

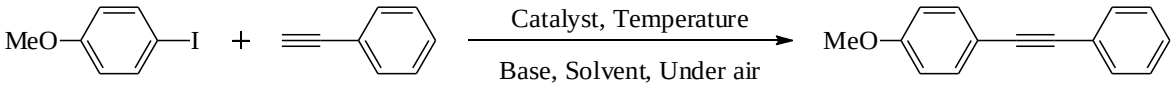
Next, we investigated the effects of precatalysts on this reaction. Precatalysts like $Pd(OAc)_2$, Pd/C, $Pd_2(dba)_3$ had the similar catalytic effect in comparison with the $PdCl_2$ which afforded 81% isolated yield (Table 1, entries 6, 9, 10 and 11). $Pd(OAc)_2$ and $Pd_2(dba)_3$ are non-supported catalysts, while Pd/C is a supported catalyst. Gratifying, they all could provide good results. More interesting, Pd/C has the advantages such as comercial availability, low cost, easy recycle by filtration. $Pd_2(dba)_3$ provided the highest yield and was chosen as the optimal precatalyst for further investigaion.

Through screening different bases, it was found that $K_3PO_4 \cdot 7H_2O$ and NaOH could afford good to excellent yields (Table 1, entries 11 and 12), while both K_2CO_3 and organic base Et_3N

delivered moderate yields (Table 1, entries 13 and 14). The results demonstrated that $K_3PO_4·7H_2O$ was the suitable base to activate this catalytic system.

The temperature was also an important factor for the reaction. Lowering the temperature significantly reduced the yields of the coupling products. For example, when lowering the temperature to 50 °C and 25 °C, the coupling products were delivered in 72% and 10% yields, respectively (Table 1, entries 15 and 16). Therefore, 80 °C was chosen as the optimal temperature.

Table 1. Screening of the optimum conditions for the Sonogashira coupling of 4-iodoanisole with phenylacetylene[a]



Entry	Catalyst	Base	Solvent (4mL)	Time (min)	Yield (%)[b]
1	$Pd(OAc)_2$	$K_3PO_4·7H_2O$	DMF/H_2O (2/2)	60	26
2	$Pd(OAc)_2$	$K_3PO_4·7H_2O$	Glycol/H_2O (2/2)	60	trace
3	$Pd(OAc)_2$	$K_3PO_4·7H_2O$	*i*-PrOH/H_2O (2/2)	60	73
4	$Pd(OAc)_2$	$K_3PO_4·7H_2O$	EtOH/H_2O (2/2)	60	77
5	$Pd(OAc)_2$	$K_3PO_4·7H_2O$	EtOH	60	44
6	$Pd(OAc)_2$	$K_3PO_4·7H_2O$	EtOH/H_2O(3/1)	60	91
7	$Pd(OAc)_2$	$K_3PO_4·7H_2O$	EtOH/H_2O(2/3)	60	28
8	$Pd(OAc)_2$	$K_3PO_4·7H_2O$	EtOH/H_2O(1/3)	60	trace
9	$PdCl_2$	$K_3PO_4·7H_2O$	EtOH/H_2O(3/1)	60	81
10	Pd/C(5%)	$K_3PO_4·7H_2O$	EtOH/H_2O(3/1)	60	90
11	$Pd_2(dba)_3$	$K_3PO_4·7H_2O$	EtOH/H_2O(3/1)	60	93
12	$Pd_2(dba)_3$	NaOH	EtOH/H_2O(3/1)	40	82
13	$Pd_2(dba)_3$	Et_3N	EtOH/H_2O(3/1)	60	42
14	$Pd_2(dba)_3$	K_2CO_3	EtOH/H_2O(3/1)	60	34
15[c]	$Pd_2(dba)_3$	$K_3PO_4·7H_2O$	EtOH/H_2O(3/1)	60	72
16[d]	$Pd_2(dba)_3$	$K_3PO_4·7H_2O$	EtOH/H_2O(3/1)	60	10

[a]Reaction conditions: 4-iodoanisole (0.5 mmol), phenylacetylene (0.75 mmol), base (1mmol), catalyst amount (0.5 mol%), 80 °C, under air. The reactions were monitored by TLC. [b]Isolated yields. [c]50 °C. [d]25 °C.

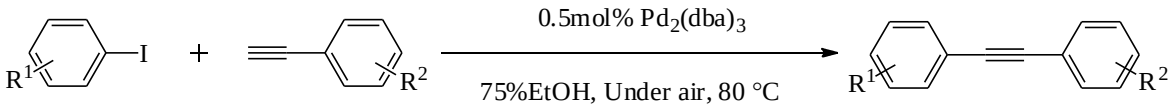
Scope and limitation of substrates

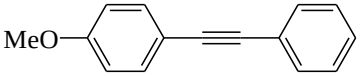
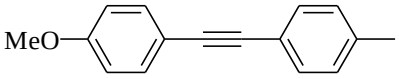
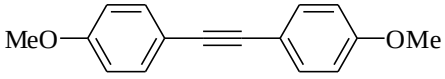
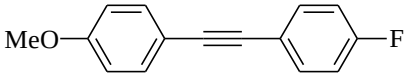
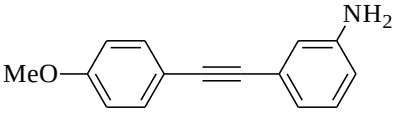
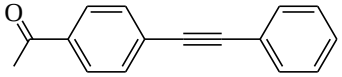
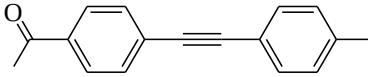
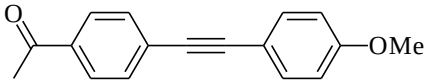
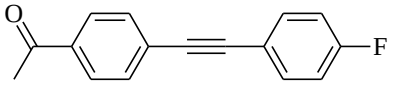
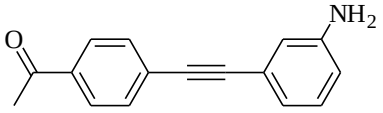
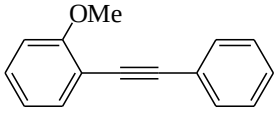
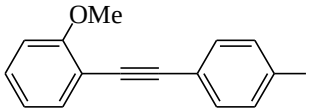
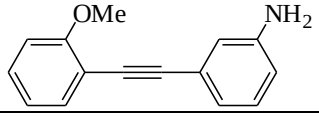
In order to investigate the feasibility of this aqueous catalytic system, a variety of aromatic terminal alkynes were subjected to the optimum conditions {0.5 mol% $Pd_2(dba)_3$, EtOH/H_2O (3/1 in volume), 1 mmol $K_3PO_4·7H_2O$, 80 °C, under air}*via* the Sonogashira reaction with aryl

iodides. The results are summarized in Table 2. Good to excellent yields were afforded for the couplings of aryl iodides with a series of substituted aromatic terminal alkynes under this phosphine-free aqueous system. It was clear that aryl iodides bearing electron-withdrawing groups completed the couplings in shorter time than those bearing electron-donating groups. The couplings of electron-rich 4-iodoanisole with phenylacetylene and 4-tolylacetylene provided the products in 93% and 90% yields in 1 h, respectively (Table 2, entries 1 and 2), which were more efficient than those in the reported phosphine-free protocols.[4e, 8a-d, 8f] It was worth noting that using 1-ethynyl-4-methoxybenzene as the coupling partner, 1,2-bis(4-methoxyphenyl)ethyne was obtained in 91% yield within 45 min, resulting in a TOF value of 243 h^{-1} (Table 2, entry 3). Nevertheless, 4-fluorophenylacetylene conducted the reaction in 81% yield in 2 h (Table 2, entry 4). The coupling of 4-iodoanisole with 3-ethynylaniline provided a 95% yield after 90 min (Table 2, entry 5). Notably, in the case of electron-poor 4'-iodoacetophenone, the couplings with various substituted aromatic terminal alkynes delivered the corresponding products rapidly in high yields (Table 2, entries 6-10), which were also far more efficient than those in reported phosphine-free systems.[8a-d, 8f] For example, the coupling of 4'-iodoacetophenone with phenylacetylene delivered a 96% yield in 20 min (Table 2, entry 6). Notably, 95% yield was achieved within 15 min using 1-ethynyl-4-methoxybenzene as the coupling partner (Table 2, entry 8). The Sonogashira reaction between electron-poor 4'-iodoacetophenone and 3-ethynylaniline delivered the cross-coupling products in 93% yield after only 10 min, resulting in a TOF of 1116 h^{-1} (Table 2, entry 10). The steric effect on the *ortho*-substituted 2-iodoanisole decreased the reactivity of the couplings with a series of aromatic terminal alkynes, consequently, relative lower yields were obtained with phenylacetylene, 4-tolylacetylene and 3-ethynylaniline (Table 2, entries 11-13).

To further investigate the scope and limitation of this phosphine-free aqueous system, a series of aliphatic terminal alkynes were coupled with 4-iodoanisole or 4'-iodoacetophenone. The results are collected in Table 3. Compared with the aromatic terminal alkynes, the coupling of aliphatic alkynes with the electron-rich 4-iodoanisole gave moderate yields (Table 3, entries 1, 3, 5, 7). The improved yields were obtained when NaOH was used in place of $K_3PO_4 \cdot 7H_2O$ (Table 3, entries 2, 4, 6, 8). According to the reported literature,[1g] the reactivity order seems to be partially related to the acidity of the alkynes, generally, the acidity of aromatic alkynes is stronger than the aliphatic alkynes. So NaOH as a strong base may be favorable for the coupling of aliphatic alkynes. Notably, the electron-poor 4'-iodoacetophenone as the coupling partner provided the products in excellent yields in short time (Table 3, entries 9-11), therefore showing high efficiency. For example, hex-5-ynenitrile and 5-chloropent-1-yne as the coupling partners gave the corresponding cross-coupling products in 92% and 95% yields within 20 min, respectively (Table 3, entries 9, 10). Noticeably, when but-3-yn-1-ol as the cross-coupling partner, the 1-(4-(4-hydroxybut-1-yn-1-yl)phenyl)ethanone was achieved in 90% yield in 15 min, which was more efficient than the aqueous *i*-propanol system (Table 3, entry 11).[8c, 8f]

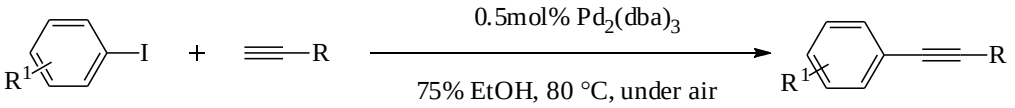
Table 2. Sonogashira reaction of aryl iodides with aromatic terminal alkynes[a]

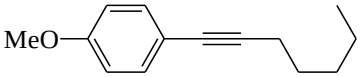
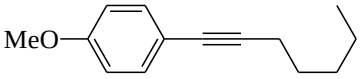
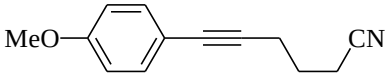
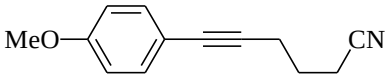
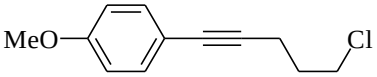
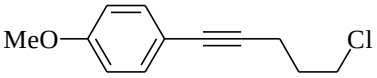
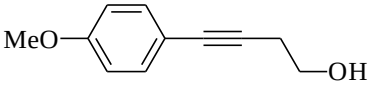
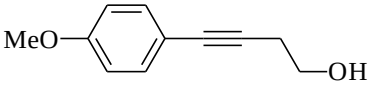
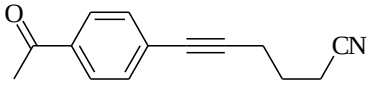
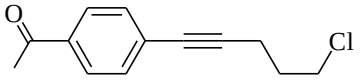
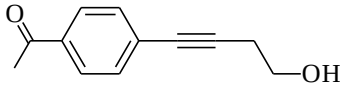


Entry	R^1	R^2	Product	Time(min)	Yield(%)[b]
1	4-OMe	H		60	93
2	4-OMe	4-Me		60	90
3	4-OMe	4-OMe		45	91
4	4-OMe	4-F		120	81
5	4-OMe	3-NH_2		90	95
6	4-COMe	H		20	96
7	4-COMe	4-Me		18	96
8	4-COMe	4-OMe		15	95
9	4-COMe	4-F		30	91
10	4-COMe	3-NH_2		10	93
11	2-OMe	H		80	81
12	2-OMe	4-Me		120	84
13	2-OMe	3-NH_2		120	74

[a]Reaction conditions: aryl iodides (0.5 mmol), terminal alkynes (0.75 mmol), $K_3PO_4 \cdot 7H_2O$ (1 mmol), $Pd_2(dba)_3$ (0.5 mol%), 80 °C, under air. The reactions were monitored by TLC. [b]Isolated yields

Table 3. Sonogashira reaction of aryl iodides with aliphatic terminal alkynes[a]



Entry	R^1	Product	Time(min)	Yield(%)[b]
1	4-OMe		120	36
2	4-OMe		120	60[c]
3	4-OMe		90	43
4	4-OMe		60	70[c]
5	4-OMe		90	51
6	4-OMe		45	72[c]
7	4-OMe		90	63
8	4-OMe		30	78[c]
9	4-COMe		20	92
10	4-COMe		20	95
11	4-COMe		15	90

[a]Reaction conditions: aryl iodides (0.5 mmol), terminal alkynes (0.75 mmol), $K_3PO_4 \cdot 7H_2O$ (1 mmol), $Pd_2(dba)_3$ (0.5 mol%), 80 °C, under air. The reactions were monitored by TLC. [b]Isolated yields. [c] NaOH was used in place of $K_3PO_4 \cdot 7H_2O$

Conclusions

In conclusion, we have developed a simple, highly efficient and phosphine-free environmentally benign protocol for the Sonogashira coupling of aryl iodides with aromatic or aliphatic terminal alkynes using a catalyst loading of 0.5 mol% under aqueous, copper-free and aerobic conditions. Further investigation on the reaction mechanism and synthetic application of this protocol are underway in our laboratory

Experimental Section

General. Unless otherwise noted, all the reactions were carried out under air. All aryl iodides and terminal alkynes were purchased from Alfa Aesar, Avocado and used without purification. Melting points were measured on a NOVEL R-3 microscopic digital melting point meter and were not corrected. ^{1}H NMR spectra were recorded on a Varian Inova 400 spectrometer. Chemical shifts are reported in ppm relative to TMS. ^{13}C NMR spectra were recorded at 100 MHz using TMS as internal standard. Mass spectroscopy data of the product were collected on a Micromass TOF mass spectrometer (EI, 70 eV). All products were isolated by short chromatography on a silica gel (200-300 mesh) column using mixtures of petroleum ether (60-90 °C) and ethyl acetate as eluents. Compounds known were characterized by comparing their melting point, ^{1}H NMR spectra to the previously reported data. New compounds were characterized by melting point, ^{1}H NMR, ^{13}C NMR spectra and high resolution mass spectrometry.

Typical experimental procedure for the Sonogashira reaction of aryl iodides with terminal alkynes

A mixture of $Pd_2(dba)_3$ (0.5 mol%), $K_3PO_4 \cdot 7H_2O$ (1 mmol), aryl iodides (0.5 mmol), terminal alkynes (0.75 mmol), ethanol (3 mL) and distilled water (1 mL) was stirred at 80 °C under air for the indicated time. After that, the mixture was added to brine (15 mL) and extracted three times with ethyl acetate (3×15 mL). The solvent was concentrated under vacuum and the product was isolated by short chromatography on a silica gel (200–300 mesh) column.

3-((4-Methoxyphenyl)ethynyl)aniline (Table 2, entry 5). Brown solid. m.p.: 75-76 °C. ^{1}H NMR: δ_H (ppm) 7.45 (d, *J* = 8.8 Hz, 2H, C_6H_4), 7.12 (t, *J* = 8.0 Hz, 1H, C_6H_4), 6.92 (d, *J* = 7.6 Hz, 1H, C_6H_4), 6.88 – 6.84 (m, 3H, C_6H_4), 6.65 – 6.63 (m, 1H, C_6H_4), 3.82 (s, 3H, OCH_3), 3.68 (s, 2H, NH_2). ^{13}C NMR: δ_C (ppm) 159.55 (C_6H_4), 146.26 (C_6H_4), 133.06 (C_6H_4), 129.27 (C_6H_4), 124.26 (C_6H_4), 121.96 (C_6H_4), 117.71 (C_6H_4), 115.48 (C_6H_4), 115.08 (C_6H_4), 113.98 (C_6H_4), 88.79 (C≡*C*), 88.29 (*C*≡C), 55.32 (OCH_3). MS (EI) *m/z* Calcd for $C_{15}H_{13}NO$: 223.0997. Found: 223.0990 (M^+).

1-(4-((3-Aminophenyl)ethynyl)phenyl)ethanone (Table 2, entry 10). Yellow solid. m.p.: 156-157°C. ^{1}H NMR: δ_H (ppm)7.93 (d, *J* = 8.0 Hz, 2H, C_6H_4), 7.59 (d, *J* = 8.4 Hz, 2H, C_6H_4), 7.15 (t, *J* = 8.0 Hz, 1H, C_6H_4), 6.96 (d, *J* = 8.0 Hz, 1H, C_6H_4), 6.88 – 6.87 (m, 1H, C_6H_4), 6.71-6.68 (m, 1H, C_6H_4), 3.72 (s, 2H, NH_2), 2.61 (s, 3H, $COCH_3$). ^{13}C NMR: δ_C (ppm) 197.36 ($COCH_3$), 146.38 (C_6H_4), 136.12 (C_6H_4), 131.70 (C_6H_4), 129.41 (C_6H_4), 128.34 (C_6H_4), 128.27 (C_6H_4), 123.33 (C_6H_4), 122.18 (C_6H_4), 117.83 (C_6H_4), 115.86 (C_6H_4), 93.05 (C≡*C*), 88.02 (*C*≡C), 26.63 ($COCH_3$). MS (EI) *m/z* Calcd for $C_{16}H_{13}NO$: 235.0997. Found: 235.1000 (M^+).

3-((2-Methoxyphenyl)ethynyl)aniline (Table 2, entry 13). Brown sticky liquid. ^{1}H NMR: δ_H (ppm) 7.48 (dd, *J* = 7.6, 1.6 Hz, 1H, C_6H_4), 7.31-7.27 (m, 1H, C_6H_4), 7.12 (t, *J* = 8.0 Hz, 1H, C_6H_4), 6.98 – 6.88 (m, 4H, C_6H_4), 6.64 (dd, *J* = 8.0, 1.6 Hz, 1H, C_6H_4), 3.90 (s, 3H, OCH_3), 3.65 (s, 2H, NH_2). ^{13}C NMR: δ_C (ppm) 159.95 (C_6H_4), 146.13 (C_6H_4), 133.59 (C_6H_4), 129.68 (C_6H_4),

129.19 (*C*$_6$H$_4$), 124.25 (*C*$_6$H$_4$), 122.24 (*C*$_6$H$_4$), 120.48 (*C*$_6$H$_4$), 118.00 (*C*$_6$H$_4$), 115.28 (*C*$_6$H$_4$), 112.58 (*C*$_6$H$_4$), 110.73 (*C*$_6$H$_4$), 93.70 (C≡*C*), 85.15 (*C*≡C), 55.86 (O*C*H$_3$). MS (EI) *m/z* Calcd for $C_{15}H_{13}NO$: 223.0997. Found: 223.1006 (M^+).

6-(4-Acetylphenyl)hex-5-ynenitrile (Table 3, entry 9). Light Yellow liquid. ^{1}H NMR: δ_H (ppm) 7.78 (d, *J* = 8.4 Hz, 2H, C$_6$*H*$_4$), 7.37 (d, *J* = 8.4 Hz, 2H, C$_6$*H*$_4$), 2.53 (t, *J* = 6.8 Hz, 2H, C*H*$_2$), 2.48 (s, 3H, COC*H*$_3$), 2.47-2.45 (m, 2H, C*H*$_2$), 1.91-1.84 (m, 2H, C*H*$_2$). ^{13}C NMR: δ_C (ppm) 197.22 (*C*OCH$_3$), 135.98 (*C*$_6$H$_4$), 131.67 (*C*$_6$H$_4$), 128.17 (*C*$_6$H$_4$), 128.12 (*C*$_6$H$_4$), 119.17 (*C*≡N), 90.87 (C≡*C*), 81.65 (*C*≡C), 26.57 (CO*C*H$_3$), 24.38 (*C*H$_2$), 18.59 (*C*H$_2$), 16.20 (*C*H$_2$). MS (EI) *m/z* Calcd for $C_{14}H_{13}NO$: 211.0997. Found: 211.0997 (M^+).

1-(4-(5-Chloropent-1-yn-1-yl)phenyl)ethanone (Table 3, entry 10). Light Yellow liquid. ^{1}H NMR: δ_H (ppm) 7.88 (d, *J* = 8.4 Hz, 2H, C$_6$*H*$_4$), 7.46 (d, *J* = 8.4 Hz, 2H, C$_6$*H*$_4$), 3.71 (t, *J* = 6.4 Hz, 2H, C*H*$_2$), 2.64 (t, *J* = 6.8 Hz, 2H, C*H*$_2$), 2.58 (s, 3H, COC*H*$_3$), 2.10-2.04 (m, 2H, C*H*$_2$). ^{13}C NMR: δ_C (ppm) 197.19 (*C*OCH$_3$), 135.87 (*C*$_6$H$_4$), 131.67 (*C*$_6$H$_4$), 128.51 (*C*$_6$H$_4$), 128.16 (*C*$_6$H$_4$), 91.94 (C≡*C*), 80.95 (*C*≡C), 43.66 (*C*H$_2$), 31.23 (*C*H$_2$), 26.54 (CO*C*H$_3$), 16.94 (*C*H$_2$). MS (EI) *m/z* Calcd for $C_{13}H_{13}ClO$: 220.0655. Found: 220.0660 (M^+).

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