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# Palladium(II) phosphine-ylide complexes as highly efficient pre-catalysts in additive- and amine-free Sonogashira coupling reactions performed under aerobic and low Pd loading conditions

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## ABSTRACT

Moisture and air-stable, robust palladacycle phosphine–ylide complexes as catalyst precursors were used in additive- and amine-free Sonogashira cross-coupling reactions. Various aryl halides were coupled with phenylacetylene in DMF, under air, in the presence of 0.001 mol % of the catalyst to afford the corresponding cross-coupled products in good to excellent yields. Application of the five-membered palladacycle [(P^C)PdCl<sub>2</sub>] (**C**<sup>1</sup>) in Sonogashira coupling reaction produced comparable catalytic activities of the seven-membered [(C^C)PdCl<sub>2</sub>] (**C**<sup>2</sup>) analogs.

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The Sonogashira coupling reaction of phenylacetylene with aryl halides catalyzed by Pd complexes in the presence of a copper reagent is a powerful tool in organic synthesis and has been widely applied to various areas such as natural product synthesis, biologically active molecules, and materials science.<sup>1</sup> In the Sonogashira coupling reaction, copper salts usually play a significant role in transmetalation.<sup>2</sup> The original Sonogashira reaction generally proceeds in the presence of a large amount of homogeneous palladium catalyst containing copper as the co-catalyst under inert conditions. It has been well-documented that the Sonogashira coupling often suffers from the Glaser-type oxidative dimerization of the alkyne substrate<sup>3</sup> as a side-reaction in the presence of a Cu(I) cocatalyst. The other limitation of Sonogashira reactions arises from the use of hazardous amines<sup>4</sup> such as piperidine or triethylamine, as solvents,<sup>5</sup> and bases in the coupling reactions.<sup>6</sup> In addition, there are only a few catalytic systems that enable the Sonogashira coupling reaction under air with a low catalyst loading.<sup>7</sup> Thus, the development of more efficient, cheap, and easily prepared catalysts, which allow the Sonogashira cross-coupling to be performed with low catalyst loadings under additive- and amine-free reaction conditions, and without the need of exclusion of air and moisture, is of high general interest. In continuation of the interest in the



Figure 1. Structures of the palladacycle phosphine-ylide complexes.

synthesis of palladacycle complexes<sup>8</sup> and the applications of these systems,<sup>9</sup> we report here additive- and amine-free, homogeneous Sonogashira reactions catalyzed under air, in DMF by two pallada-cycle phosphine complexes that we recently developed (Fig. 1).<sup>10</sup>

Complexes  $C^1$  and  $C^2$  were evaluated in the additive- and amine-free Sonogashira coupling reactions of aryl halides with phenylacetylene. We first investigated the effect of different solvents (Table 1, entries 1–7) on the model reaction of 4-bromobenzaldehyde with phenylacetylene catalyzed by 0.001 mol % of catalyst  $C^2$ , without copper iodide under air. K<sub>2</sub>CO<sub>3</sub> was used as a base in this reaction. The solvent had a dramatic influence on the product formation. Generally moderate product yields were observed when the reactions were performed in solvents of low polarity, such as 1,4-dioxane and toluene. High yields were observed when highly polar solvents, such as acetonitrile,

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dimethylformamide (DMF), *N*-methylpyrrolidone (NMP), methanol, or H<sub>2</sub>O were used as the reaction medium. The yield of cross-coupled product was reduced as the polarity of the organic solvent decreased. As shown in Table 1, DMF gave the highest yield (entry 7, 90%) after 3.5 h at 130 °C under copper-free conditions.

We next investigated the influence of various bases (Table 1, entries 7–13) on the model system using 0.001 mol % of catalyst  $C^2$ under air. Under identical reaction conditions, bases such as K<sub>2</sub>CO<sub>3</sub>, Et<sub>3</sub>N, Cs<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, NaOAc, and NaF led to considerable variation in the isolated yields. However, only K<sub>2</sub>CO<sub>3</sub> and Cs<sub>2</sub>CO<sub>3</sub> gave acceptable results with DMF as the solvent. Based on the results shown in Table 1, K<sub>2</sub>CO<sub>3</sub> was the best choice.

Various catalyst concentrations were also tested and the results are shown in Table 2. A control experiment indicated that the coupling reaction did not occur in the absence of a catalyst (entry 1). A catalyst loading of 0.001 mol % was found to be optimum (Table 2, entries 4 and 8).

Using the optimized conditions, we examined the scope of the reaction of phenylacetylene with various aryl halides using  $[(P^{C})PdCl_{2}]$  (**C**<sup>1</sup>) as the catalyst and the results are shown in Table 3. High yields of diaryl acetylenes were obtained in reactions with electron-poor aryl halides, while low product yields were obtained in the reactions with electron-rich aryl halides.<sup>11</sup>

As expected, the coupling of phenylacetylene with iodides and bromides led to the desired products in good to high yields (Table 3, entries 1–12). In particular, the reactions of aryl iodides substituted with electron-withdrawing groups occurred in high yield at 130 °C (Table 3, entries 2, 3, and 5). Electron neutral iodobenzene was converted into the corresponding product in 81% yield after 6 h. 4-Iodotoluene as a deactivated aryl iodide clearly gave the corresponding product in 80% yield, after 7 h at 130 °C and did not produce any side products. In the case of activated bromides, longer reaction times were required relative to activated aryl iodides in order to obtain good yields (Table 3, entries 7, 8, and 10).

When less reactive aryl bromides with electron-donating groups were used, the coupling product was obtained in an acceptable yield after a longer reaction time of 10 h (Table 3, entry 9, 72%). As expected, satisfactory results were obtained with 2-bromothiophene and 1-bromonaphthalene (Table 3, entries 11 and 12). The catalyst effect was also evident for chlorides, where only those substituted with electron-withdrawing groups gave acceptable yields of the coupling products (Table 3, entries 14 and 16). A non-activated aryl chloride gave a moderate yield in the coupling

#### Table 1

Optimization of the base and solvent for the copper-free Sonogashira reaction of 4-bromobenzaldehyde with phenylacetylene<sup>a</sup>

$H = \frac{\operatorname{Cat.} (0.001 \operatorname{mol}\%)}{\operatorname{Base, Solvent}} + H = \frac{\operatorname{Cat.} (0.001 \operatorname{mol}\%)}{\operatorname{Base, Solvent}} + H$					
Entry	Base	Solvent	Time (h)/Temp (°C)	Yield <sup>b</sup> (%)	
1	K <sub>2</sub> CO <sub>3</sub>	1,4-Dioxane	4/110	60	
2	K <sub>2</sub> CO <sub>3</sub>	NMP	3/130	71	
3	K <sub>2</sub> CO <sub>3</sub>	MeOH	8/60	40	
4	K <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN	8/80	53	
5	K <sub>2</sub> CO <sub>3</sub>	Toluene	4/110	65	
6	K <sub>2</sub> CO <sub>3</sub>	H <sub>2</sub> O	24/100	Trace	
7	K <sub>2</sub> CO <sub>3</sub>	DMF	3.5/130	90	
8	Et <sub>3</sub> N	H <sub>2</sub> O	12/100	24	
9	Cs <sub>2</sub> CO <sub>3</sub>	DMF	3.5/130	75	
10	Na <sub>2</sub> CO <sub>3</sub>	DMF	3.5/130	52	
11	NaOAc	DMF	12/130	47	
12	NaF	DMF	12/130	32	
13	Et <sub>3</sub> N	DMF	24/130	12	

<sup>a</sup> Reaction conditions: 4-bromobenzaldehyde (1 mmol), phenylacetylene (1.3 mmol), catalyst **C<sup>2</sup>** (0.001 mol %), base (2.5 mmol), solvent (2 ml), 130 °C, under air.

<sup>b</sup> Isolated yield.

#### Table 2

The effect of the amount of catalyst on the Sonogashira coupling of 4-bromobenzaldehyde with phenylacetylene<sup>a</sup>

$\begin{array}{c ccccc} 1 & None & -\\ 2 & C^{1}(0.1) & 90\\ 3 & C^{1}(0.01) & 90\\ 4 & C^{1}(0.01) & 84\\ \end{array}$	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	
3 $C^{1}(0.01)$ 90	
$C^{1}(0.001)$ 84	
4 C (0.001) 04	
5 $C^1(0.005)$ 85	
6 $C^{2}(0.1)$ 95	
7 $C^2(0.01)$ 91	
8 $C^2(0.001)$ 90	
9 $C^2(0.005)$ 90	

 $^a$  Reaction conditions: 4-bromobenzaldehyde (1 mmol), phenylacetylene (1.3 mmol),  $K_2CO_3$  (2.5 mmol), DMF (2 ml), 3.5 h, 130 °C, under air.

<sup>b</sup> Isolated yields.

## Table 3

Copper-free Sonogashira reactions of aryl halides with phenylacetylene catalyzed by precursor  ${\bm C}^{1a}$ 



Entry	Ar-X	Product <sup>b</sup>	Time (h)	Yield <sup>c</sup> (%)
1		1a	6	81
2	онс	1b	4	85
3		1c	4	84
4		1d	7	80
5	Hacoc	1e	4.5	84
6	Br	1a	8	78
7	онсВг	1b	5	84
8	D <sub>2</sub> N-Br	1c	5	83
9	H <sub>3</sub> C Br	1d	10	72
10	H <sub>3</sub> COC-Br	1e	5.5	80
11	Br	1f	5	75
12	Br	1g	8	76
13	Ci Ci	1a	12	67
14	онсСі	1b	10	74
15	H <sub>3</sub> cCI	1d	16	58 (66) <sup>d</sup>
16	H <sub>3</sub> cocci	1e	10	70

<sup>a</sup> Reaction conditions: aryl halides (1 mmol), phenylacetylene (1.3 mmol), catalyst precursor  $C^1$  (0.001 mol %), K<sub>2</sub>CO<sub>3</sub> (2.5 mmol), DMF (2 ml), 130 °C, under air. <sup>b</sup> For characterization of the corresponding products (**1a–1g**) refer to Supple-

mentary data.

<sup>c</sup> Isolated yield.

 $^{\rm d}\,$  Using 0.01 mol % of the catalyst  ${\bf C^1}.$ 

reaction using a 0.01 mol% catalyst loading and longer reaction time (Table 3, entry 15, 58%).

We next examined the copper-free reactions of aryl halides catalyzed by 0.001 mol % of  $[(C^{A}C)PdCl_2]$  (**C**<sup>2</sup>) (Table 4).

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Electron-neutral, electron-rich, and electron-poor aryl iodides reacted with phenylacetylene to generate the corresponding cross-coupling products in excellent yields (Table 4, entries 1–5). The mononuclear phosphine–ylide palladacycle complexes catalyzed the copper-free reactions such that all of the aryl halides were converted into the desired products within 2.5–10 h, which is excellent catalytic efficiency compared to the results of the previous homogenous system.<sup>12</sup> Interestingly, the Sonogashira coupling of phenylacetylene with aryl bromides bearing electron-donating and electron-withdrawing groups gave the corresponding biarylacetylenes in excellent yields (Table 4, entries 7–10). The electronically neutral bromobenzene (Table 4, entry 6) produced a good yield of the desired product. 2-Bromothiophene and 1-bromonaph-thalene were also efficient substrates (Table 4, entries 11 and 12).

We next investigated the coupling of various aryl chlorides with phenylacetylene. The coupling products of 4-chlorobenzaldehyde and 4-chloroacetophenone with phenylacetylene were obtained in good yields by using 0.001 mol % of  $C^2$ . However, for chlorobenzene, catalyst  $C^2$  showed low activity (Table 4, entry 13). For 4-methylchlorobenzene with the as electron-donating group, a low yield was observed (Table 4, entry 15, 60%). Increasing the catalyst loading to 0.01 mol % gave a moderate yield for

## Table 4

Copper-free Sonogashira reactions of aryl halides with phenylacetylene catalyzed by precursor  ${\bf C}^{{\bf 2}a}$ 



Entry <sup>b</sup>	Ar-X	Time (h)	Yield <sup>c</sup> (%)
1		4.5	87
2	онс	3	91
3		3	88
4	H <sub>s</sub> c	5	86
5	H3COC1	3.5	87
6	Br	6.5	84
7	OHC Br	3.5	90
8	b <sub>2</sub> NBr	3	87
9	H <sub>3</sub> C Br	8	80
10	H <sub>3</sub> COCBr	5	84
11	Br	2.5	90
12	Br	7	85
13	Ci	9	71
14	онс	8	76
15	H <sub>3</sub> C Ci	10	60 (73) <sup>d</sup>
16	H <sub>3</sub> cocCl	7	76

<sup>a</sup> All reactions were carried out under air.

<sup>c</sup> Isolated yield.

<sup>d</sup> Using 0.01 mol % of the catalyst **C**<sup>2</sup>.

4-methylchlorobenzene (Table 4, entry 6, 73%) without addition of Cu(I) as a co-catalyst. As can be seen in Tables 3 and 4, when the reactions with 4-chloroacetophenone were carried out at 130 °C, catalyst **C**<sup>1</sup> gave the coupling product in 70% yield (Table 3, entry 16), while C<sup>2</sup> gave a 76% product yield (Table 4, entry 16), suggesting that  $C^2$  again shows higher catalytic activity than  $C^1$ . Increasing the reactivity of the catalytic system by using bulkier phosphine ligands has been shown often as an appropriate way to perform copper-free Sonogashira reactions. Palladium systems modified with a bulky and electron rich phosphine ligand, can be used to provide unusually high activity in Sonogashira coupling reactions.<sup>1c,6b,13</sup> It was found that bulky and symmetrical phosphorus ylide containing complex  $C^2$  was the most active catalyst in these C-C cross-coupling reactions. Electron-rich compounds favor the oxidative addition step, whereas the steric bulkiness favors the formation of low-coordinate and highly active palladium complexes.<sup>14</sup>

Although acetylene homo-coupling reactions are generally useful in synthetic applications,<sup>15</sup> the formation of homo-coupling products while targeting cross-coupling is undesirable. This is because the terminal acetylene is either very expensive or is synthesized via several steps. Therefore, the formation of a dimer is considered wasteful. In this protocol, no copper salt was used and the undesired formation of oxidative homo-coupling diyne products was avoided.

Electrochemistry is a convenient technique to detect Pd(0) complexes that are generated in situ from Pd(II) complexes.<sup>16</sup> Electrochemical studies of  $C^1$  and  $C^2$  were carried out by cyclic voltammetry (CV) in acetonitrile, containing 0.1 M tetrabutylammonium tetrafluoroborate (TBATFB) as the supporting electrolyte with Au as the working electrode and Pt wire as the counter electrode. All the potentials were referenced to Ag/AgCl reference electrode. Cyclic voltammograms were used to elucidate the oxidation states of Pd in the catalytic process (Fig. 2).

For complex  $C^1$  the cathodic potential peak corresponding to the redox pair appeared at -0.83 V versus Ag/AgCl. The reduction was due to a one-electron transfer process. When the potential was scanned further in the cathodic direction, a second cathodic potential peak at -1.03 V was observed, which corresponds to the Pd(I)/Pd(0). Another cathodic peak was observed at -1.49 V corresponding to reduction of the nitro group.<sup>17</sup> For  $C^2$ , the cyclic voltammogram displayed two reduction peaks at -0.81 V and -1.08 V, respectively (Fig. 2). The first peak was assigned to the Pd(II)/Pd(I). Second was assigned to the reduction of Pd(I)/ Pd(0).<sup>9b,10a,18</sup> In addition, the CV of the  $C^2$  exhibited an irreversible



**Figure 2.** Cyclic voltammograms of 1 mM of  $C^1$  and  $C^2$  in acetonitrile containing 0.1 M TBATFB as the supporting electrolyte. Scan rate = 100 mV/s.

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<sup>&</sup>lt;sup>b</sup> The reaction progress was monitored by thin layer chromatography (TLC).

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Table	5
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Entry	Ar–X	[Pd] catalyst	mol %	Conditions	Yield (%)
1	C <sub>6</sub> H <sub>5</sub> -I	$[(P^{C})_{2}Pd_{2}Cl_{2}]^{20a}$	1	Et₃N, ionic liquid, <sup>a</sup> under air, 80 °C, 1 h	41-56
2	4-COMe-C <sub>6</sub> H <sub>4</sub> -Br	[Pd(dmba)Cl(PTA)] <sup>b,20b</sup>	2.5	Cs <sub>2</sub> CO <sub>3</sub> , CH <sub>3</sub> CN, under air, 80 °C, 24 h	100
3	4-COMe-C <sub>6</sub> H <sub>4</sub> -Br	$[(PPh_3)_2PdCl_2]^{21a}$	4	Piperidine, under air, 70 °C, 10 min	99
4	4-COMe-C <sub>6</sub> H <sub>4</sub> -Cl	$[(PPh_3)_2PdCl_2], P^tBu_3^{21b}$	0.5	Cs <sub>2</sub> CO <sub>3</sub> , DMF, DBU, <sup>c</sup> under nitrogen, 150 °C, 10 min	93
5	4-COMe-C <sub>6</sub> H <sub>4</sub> -Cl	$[Pd(C_{3}H_{5})Cl]_{2}/Fc(P)_{2}^{t}Bu(P^{i}Pr)^{d,22}$	0.004	K <sub>2</sub> CO <sub>3</sub> , DMF, under argon, 130 °C, 20 h	82
6	C <sub>6</sub> H <sub>5</sub> -Br	$[(N^{C})_{2}Pd_{2}Br_{2}]^{23}$	0.8	Piperidine, NMP, under air, 100 °C, 10 h	50
7	C <sub>6</sub> H <sub>5</sub> -Br	$[(PPh_3)_2PdCl_2]^{e,24a}$	3	KO <sup>t</sup> Bu, THF, under argon, 65 °C, 2 h	91
8	4-Me-C <sub>6</sub> H <sub>4</sub> -Br	[Pd] <sup>f,24b</sup>	1	Cs <sub>2</sub> CO <sub>3</sub> , DMF, CuI, PPh <sub>3</sub> , under air, 80 °C, 24 h	90
9 <sup>g</sup>	C <sub>6</sub> H <sub>5</sub> -Br	$[(C^{C})PdCl_2](C^2)$	0.001	K <sub>2</sub> CO <sub>3</sub> , DMF, under air, 130 °C, 6.5 h	84 (8 h/78%) <sup>h</sup>
10	4-COMe-C <sub>6</sub> H <sub>4</sub> -Cl	$[(C^{C})PdCl_2](C^2)$	0.001	K <sub>2</sub> CO <sub>3</sub> , DMF, under air, 130 °C, 7 h	76 (10 h/70%) <sup>h</sup>
11	4-COMe-C <sub>6</sub> H <sub>4</sub> -Br	$[(C^{A}C)PdCl_{2}] (\mathbf{C}^{2})$	0.001	K <sub>2</sub> CO <sub>3</sub> , DMF, under air, 130 °C, 5 h	84 (4.5 h/84%) <sup>h</sup>

<sup>a</sup> [bmim][PF<sub>6</sub>] and [bmim][PF<sub>4</sub>].

<sup>b</sup> PTA = 1,3,5-triaza-7-phosphaadamantane.

<sup>c</sup> 1,8-Diazabicyclo[5.4.0]undec-7-ene.

<sup>d</sup> Palladium tridentate ferrocenyl phosphine complex.

<sup>e</sup> Used with 18-crown-6 and dihydroimidazolium hexafluorophosphate salt.

<sup>f</sup> Carbamoyl-substituted N-heterocyclic carbene Pd(II) complexes.

<sup>g</sup> This work (entries 9–11).

<sup>h</sup> Using [(P^C)PdCl<sub>2</sub>] (**C**<sup>1</sup>) as the catalyst.

reduction peak at -1.42 V corresponding to reduction of the nitro group. Therefore, we conclude that the reaction mechanism occurs via reduction of Pd(II) to Pd(0) in the Sonogashira cycle.

To evaluate the homogeneous nature of the catalysts and proposed reduction of the palladium(II) phosphine–ylide complexes to Pd(0) species, the mercury drop test was utilized, since mercury leads to amalgamation of the surface of a heterogeneous catalyst. In contrast, Hg(0) is not expected to have a poisoning effect on homogeneous palladium complexes.<sup>19</sup> When two drops of Hg(0) were added to the reaction mixture of 4-bromobenzaldehyde and phenylacetylene under the optimized conditions and heated using an oil bath, the conversion of the reaction was not affected, which suggests that the catalysis is homogeneous in nature (please see Supplementary data: Table S1). The fact that metallic Hg does not stop the catalysis is a good indication that no metallic Pd is being produced. The data obtained confirmed that the Pd(0):Pd(II) cycle was accruing.

Although several catalytic systems have been reported to support additive- and amine-free Sonogashira C-C coupling reactions, homogeneous catalyst precursors of the type  $[(P^{C})PdCl_{2}](C^{1})$  and  $[(C^{C})PdCl_{2}]$  ( $C^{2}$ ) are novel with respect to the P and CH phosphorus ylide environment. A comparison of palladacycles  $C^1$  and  $C^2$ with other similar palladacycle systems in Sonogashira reactions is presented in Table 5. Utilizing the conventional copper-free Sonogashira cross-coupling reactions of phenylacetylene with various aryl halides, comparisons are made of the efficiencies of the catalyst systems based on palladacycle bisphosphine monoylide  $(C^1)$ , bisphosphine bisylide  $(C^2)$  with monophosphine (Table 5, entries 1 and 2),<sup>20</sup> bisphosphine (Table 5, entries 3 and 4),<sup>21</sup> and tetraphosphine (Table 5, entry 5)<sup>22</sup> Pd(II) complexes. Of note is that the best results for the coupling of phenylacetylene with aryl halides were obtained with phospha-palladacycles (Table 5, entry 6),<sup>23</sup> or with palladacycles modified with carbenes (Table 5, entries 7 and 8),<sup>24</sup> or phosphorus containing ligands (Table 5, entry 4).<sup>21b</sup> This might be rationalized by the extra stability provided by these ligands for the stabilization of the low-ligated catalytically active Pd(0) species involved in the main catalytic cycle.<sup>21</sup>

The ease of preparation of the complexes as homogeneous catalysts, their high solubility in organic solvents, low catalyst loading, and stability toward air make them ideal complexes for Sonogashira coupling. This method proved successful in most cases to give the product in >99% purity. In all of the successful reactions, the <sup>1</sup>H and <sup>13</sup>C NMR data of the products indicated no homocoupling diyne products.

## General experimental procedure for the Sonogashira crosscoupling

A mixture of an aryl halide (1 mmol), phenylacetylene (1.3 mmol), catalyst (0.001 mol %),  $K_2CO_3$  (2.5 mmol), and DMF (2 ml) was heated to 130 °C. The mixture was then cooled to room temperature and the solvent was removed under reduced pressure. The combined organic extracts were washed with brine and dried over CaCl<sub>2</sub> or MgSO<sub>4</sub>. The solvent was evaporated and liquid residues were purified by silica gel column chromatography (*n*-hexane:EtOAc, 80:20) and solid residues were purified by recrystallization from EtOH and H<sub>2</sub>O. Products were identified by comparison of their <sup>1</sup>H and <sup>13</sup>C NMR spectral data those reported in the literature.<sup>26-35</sup>

In conclusion, we have used five-membered complex  $C^1$  (containing P,C-donors ligand) and seven-membered complex  $C^2$  (containing C,C-donors ligand) as efficient and well-defined catalysts for the Sonogashira coupling of various aryl halides. Also, we have developed optimized conditions for additive- and amine-free Sonogashira reactions catalyzed by these palladacycle complexes under aerobic conditions. The catalysts show high activity, and offer many practical advantages such as low catalyst loading and air stability.

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## Supplementary data

Supplementary data (<sup>1</sup>H and <sup>13</sup>C NMR spectra of Sonogashira coupling reaction products and the results of Sonogashira cross-coupling reactions catalyzed under mercury drop conditions) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2013.06.064.

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