

# CO<sub>2</sub> as Both a Selective Agent and Reaction Media in Palladium-Catalyzed Reductive Ullmann-Type Coupling Reaction<sup>†</sup>

LI, Jin-Heng\*(李金恒) XIE, Ye-Xiang(谢叶香)

Key Laboratory of Chemical Biology & Traditional Chinese Medicine Research, College of Chemistry and Chemical Engineering, Hunan Normal University, Changsha, Hunan 410081, China

Carbon dioxide as both a selective agent and reaction media in the palladium-catalyzed Ullmann-type coupling has been described. The results showed that aryl chlorides could be easily activated in the presence of carbon dioxide and the chemoselectivity shifted toward the palladium-catalyzed Ullmann-type coupling reaction. In liquid carbon dioxide, homocoupling reactions of aryl halides, including less reactive aryl chlorides, were carried out smoothly in moderate to good yields using Pd/C, zinc, and H<sub>2</sub>O as the catalytic system at room temperature.

**Keywords** carbon dioxide, a selective agent, reaction media, palladium, Ullmann-type coupling reaction, aryl halide

Recently, much attention has been attracted on the use of carbon dioxide (liquid and supercritical) instead of the conventional organic solvents.<sup>1,2</sup> For environmental reasons, CO<sub>2</sub> is a preferred reaction medium. In addition, the advantages of CO<sub>2</sub> as the reaction media include the high solubility of gaseous reactants, rapid diffusion of solutes, and possible weakening of the solvation around the reactants. All the properties can provide substantial selectivity and rate enhancement. As part of our continuing program in the application of carbon dioxide to organic synthesis,<sup>1a-f</sup> we report here an improved environmental benign Ullmann coupling method for the synthesis of symmetric biaryls.

The Ullmann coupling reaction,<sup>3-7</sup> generally using copper as catalyst,<sup>3</sup> is one of the most important methods for the formation of carbon-carbon bond in synthetic organic chemistry. Recently it attracts much attention on the combination of palladium and reductive reagents as the catalytic systems instead of copper due to their mildness and efficiency.<sup>5-7</sup> Li and Venetrakaman have reported that the coupling reaction of aryl iodides and bromides could be carried out smoothly in the presence of Pd/C and zinc in water. The addition of co-solvent (acetone)<sup>5a</sup> or phase-transfer catalyst (PTC: crown ether)<sup>5b</sup> could improve the coupling, however, aryl chlorides were inert. Sasson and coworkers<sup>5c</sup> have also described that aryl chlorides could be coupled in the presence of Pd/C, Zn, and PTC (PEG-400 or TBAB) in water, but both base and high reaction temperature (60—120 °C) were required. Very recently, we have reported the CO<sub>2</sub>-promoted Pd/C and zinc-mediated Ullmann coupling reaction in water.<sup>5d</sup> In the presence of

Pd/C, zinc and CO<sub>2</sub> (1 MPa), various aryl halides were coupled to afford the corresponding symmetric biaryls in excellent yields using H<sub>2</sub>O as the reaction solvent. For example, for the Pd/C and zinc-mediated coupling of iodobenzene in H<sub>2</sub>O, only 27% yield of biphenyl was isolated without CO<sub>2</sub>, whereas 100% yield was obtained in the presence of 1.0 MPa of CO<sub>2</sub>. However, the role of CO<sub>2</sub> in the palladium-catalyzed Ullmann coupling reaction needed to be further explored. Thus, we decided to apply the Ullmann coupling to liquid CO<sub>2</sub>. In liquid carbon dioxide, we found that not only various aryl iodides and bromides, but also aryl chlorides, less reactive compounds, were coupled in moderate to good yields in the presence of Pd/C, zinc, and H<sub>2</sub>O at room temperature. Herein, we report the details of these reactions.

Coupling of iodobenzene was firstly chosen as a model reaction to evaluate the palladium-catalyzed Ullmann coupling reaction in liquid CO<sub>2</sub>, and the results are summarized in Table 1. The results showed that both H<sub>2</sub>O and CO<sub>2</sub> could affect the coupling of iodobenzene (**1a**) to some extent in the presence of Pd/C and zinc (Entries 1, 2, and 5). Without H<sub>2</sub>O, only 14% of **1a** was consumed and 12% yield of the corresponding coupled product **2a** (biphenyl) was isolated after overnight in liquid CO<sub>2</sub> (Entry 1). On the other hand, in the absence of CO<sub>2</sub>, a previous study<sup>5a</sup> of Pd/C and zinc in Ullmann type coupling reaction of **1a** reported a 21% yield of the desired coupling product **2a** using H<sub>2</sub>O as solvent. Indeed, without CO<sub>2</sub>, only 27% yield of **2a** was found in the presence of Pd/C (5%, 400 mg), Zn (260 mg) and H<sub>2</sub>O (1 mL) (Entry 2). Interestingly, the presence of both H<sub>2</sub>O and liquid CO<sub>2</sub> could improve the coupling.

\* E-mail: jhli@mail.hunnu.edu.cn

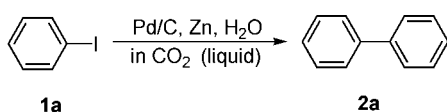
Received March 29, 2004; revised and accepted August 18, 2004.

Project supported by the National Natural Science Foundation of China (No. 20202002), Hunan Province Department of Education (No. 02C211) and Hunan Normal University (2001).

<sup>†</sup>Dedicated to Professor Chengye Yuan on the occasion of his 80th birthday.

The yield of **2a** was increased to 58% when the reaction was mediated by Pd/C zinc and H<sub>2</sub>O in liquid CO<sub>2</sub> (entry 5).<sup>7</sup> Trace of **2a** was isolated in the absence of zinc (Entry 3). The yield of **2a** was decreased to some extent with either increasing or decreasing the loadings of Pd/C (Entries 4 and 6). No coupled product **2a** was isolated using HOAc as the reaction solvent (Entry 7). To check the basic mass balance of the coupling, the dried extraction not separated of Entry 5 was directly detected by GC-MS analysis. The analysis results showed that **1a** was converted into 60% yield of **2a** and 40% yield of benzene.

**Table 1** Palladium-catalyzed Ullmann coupling of **1a** in liquid CO<sub>2</sub><sup>a</sup>



Entry	5% Pd/C/mg	Isolated yield/%
1 <sup>b</sup>	400	12
2 <sup>c</sup>	400	27
3 <sup>d</sup>	400	trace
4	200	44
5	400	58
6	600	53
7 <sup>e</sup>	400	—

<sup>a</sup> Reaction conditions: **1a** (2 mmol), Pd/C (5% w/w), Zn (260 mg), H<sub>2</sub>O (1 mL), CO<sub>2</sub> (6 MPa) at room temperature overnight. <sup>b</sup> Without H<sub>2</sub>O, conversion of **1a** was 14% determined by GC analysis. <sup>c</sup> Without CO<sub>2</sub>. <sup>d</sup> Without zinc. <sup>e</sup> HOAc (5 mL) instead of liquid CO<sub>2</sub> as the reaction solvent.

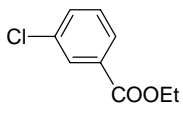
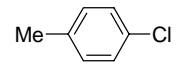
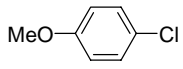
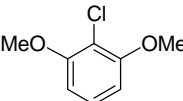
In liquid CO<sub>2</sub>, various other aryl halides **1b—1q** including less reactive aryl chlorides were coupled in moderate to good yields, the results are summarized in Table 2. In the presence of Pd/C (5%, 400 mg), Zn (260 mg) and H<sub>2</sub>O (1 mL), couplings of aryl iodides **1b—1f** and bromides **1h—1k** with different groups were carried out smoothly in moderate to high yields in liquid CO<sub>2</sub> overnight. Unfortunately, coupling of **1g** bearing an electron-withdrawing group failed. For couplings of aryl chlorides **1l—1q**, however, more loadings of Pd/C were required to improve the chemoselectivity. In the presence of 400 mg of Pd/C, substrates **1l** and **1m** afforded the corresponding coupled products **2a** and **2f** in 21% and 30% yields, respectively, whereas 50% and 92% yields of **2a** and **2f** were obtained, respectively, with increasing amount of Pd/C to 600 mg. Other aryl chlorides **1n—1q** were coupled smoothly in the presence of 600 mg of Pd/C (Entries 15—18).

Based upon the results, two points should be noted: (a) the presence of CO<sub>2</sub> and H<sub>2</sub>O played a critical role in the reaction. In the absence of CO<sub>2</sub>, selectivity toward the coupling was rather low, and no coupling reaction

**Table 2** Palladium-catalyzed Ullmann coupling reaction in liquid CO<sub>2</sub><sup>a</sup>

Entry	Aryl halide	Isolated yield/%
1	<b>1b</b>	60 ( <b>2b</b> )
2	<b>1c</b>	42 ( <b>2c</b> )
3	<b>1d</b>	54 ( <b>2d</b> )
4	<b>1e</b>	98 ( <b>2e</b> )
5	<b>1f</b>	48 ( <b>2f</b> )
6 <sup>b</sup>	<b>1g</b>	NR
7	<b>1h</b>	49 ( <b>2a</b> )
8	<b>1i</b>	53 ( <b>2d</b> )
9	<b>1j</b>	81 ( <b>2j</b> )
10	<b>1k</b>	37 ( <b>2k</b> )
11	<b>1l</b>	21 ( <b>2a</b> )
12 <sup>c</sup>	<b>1l</b>	50 ( <b>2a</b> )
13 <sup>d</sup>	<b>1m</b>	30 ( <b>2e</b> )
14 <sup>c</sup>	<b>1m</b>	92 ( <b>2e</b> )

Continued

Entry	Aryl halide		Isolated yield/%
15 <sup>c</sup>		<b>1n</b>	43 ( <b>2n</b> )
16 <sup>c</sup>		<b>1o</b>	43 ( <b>2b</b> )
17 <sup>c</sup>		<b>1p</b>	43 ( <b>2d</b> )
18 <sup>c</sup>		<b>1q</b>	43 ( <b>2k</b> )

<sup>a</sup> Reaction conditions: **1** (2 mmol), Pd/C (5%, 400 mg), Zn (260 mg), H<sub>2</sub>O (1 mL), CO<sub>2</sub> (6 MPa) at room temperature overnight.

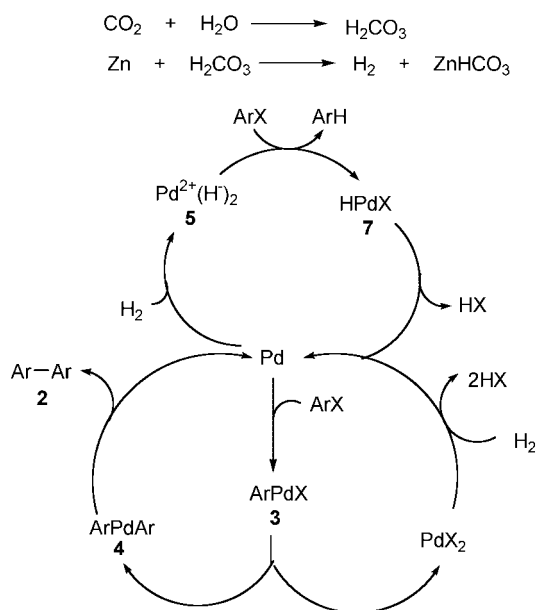
<sup>b</sup> NR=No reaction. <sup>c</sup> Pd/C (5%, 600 mg). <sup>d</sup> Conversion of **1m** was 31% determined by GC analysis.

was observed for aromatic chlorides. Similarly, in the absence of H<sub>2</sub>O, the reaction was ineffective; (b) The selectivity toward the coupling in liquid CO<sub>2</sub> was identical to the previous reports of Li and Ventrakaman on using Pd/C, Zn, promoter (co-solvent or PTC) and H<sub>2</sub>O as the catalytic system. In liquid CO<sub>2</sub>, however, not only various aryl iodides and bromides but also aryl chlorides, less reactive compounds, could be coupled in moderate to good yields without any other promoters.

Either a direct metal-to-metal electron transfer or the reduction of palladium intermediate *in situ* by hydrogen gas is the main difference between two plausible mechanisms that were proposed by Li<sup>5a,5b</sup> and Sasson,<sup>5c</sup> respectively. It was noticed that Li's reaction conditions were neutral and Sasson's were basic, but the present reaction conditions were acidic. So the present reaction might proceed via the reduction of palladium intermediate *in situ* by hydrogen gas pathway, which is proposed as outlined in Scheme 1. It is well-known that carbon dioxide in water generates carbonic acid (H<sub>2</sub>CO<sub>3</sub>) readily to lower the pH value of the reaction systems, so the first step might be the reaction of CO<sub>2</sub> with H<sub>2</sub>O to yield H<sub>2</sub>CO<sub>3</sub>, a Brønsted acid, which then afforded H<sub>2</sub> by reacting with Zn. In the presence of H<sub>2</sub>, Pd(0) might work with either aryl halide or H<sub>2</sub> to give intermediate **3** (ArPdX) and intermediate **5** (Pd<sup>2+</sup>(H<sup>-</sup>)<sub>2</sub>), respectively. Intermediate **3** afforded intermediate **4** and PdX<sub>2</sub>. Intermediate **4** then released **2** and regenerated the active Pd(0) species. PdX<sub>2</sub> reacted with H<sub>2</sub> to regenerate the active Pd(0) species, too. At the same time, aryl halides were reduced by intermediate **5** to give ArH.

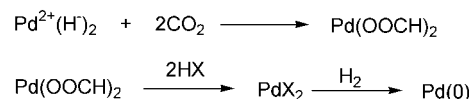
In Ref. 5c, NaOH was added to reduce the concentration of intermediate **5**, resulting in the selectivity toward coupling. Although there is no direct evidence to support the following hypothesis in Scheme 2, it is

Scheme 1



believed that similar to NaOH, CO<sub>2</sub> might be used to decrease the concentration of intermediate **5** to affect the selectivity of the coupling besides the acidity of CO<sub>2</sub>.<sup>8</sup> To elucidate this role, it can be assumed that the insertion of CO<sub>2</sub> into Pd-H bond might take place to form Pd(OOCH)<sub>2</sub>, followed by reacting with HX to afford the active Pd species resulting in selectivity toward coupling.<sup>9</sup>

Scheme 2



In conclusion, we have developed a general and environmental benign protocol to synthesize symmetric biaryls. In liquid CO<sub>2</sub>, various aromatic halides including less reactive aromatic chlorides were coupled in moderate to good yields. Further efforts associated with the use of carbon dioxide as reaction media in organic synthesis are in progress in our laboratory.

## Experimental

All <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker AMX-400 or 300 spectrometer with CDCl<sub>3</sub> as solvent. All reagents were used directly as obtained commercially. All products **2** are known.<sup>5-7</sup>

### Typical experimental procedure for the Ullmann coupling

ArX **1** (2 mmol) was added to a mixture of Pd/C (5%, 400 mg, 0.18 mmol), zinc powder (260 mg, 4 mmol), and H<sub>2</sub>O (1 mL) in HF-25 autoclave. Liquid CO<sub>2</sub> was then transferred into the autoclave to 6 MPa. The reaction mixture was stirred at room temperature overnight.

After the gas was vented, the residue was extracted with ethyl ether and purified by flash column chromatography to give **2** (hexane/ethyl acetate). Under the above reaction conditions, all ArX **1** were consumed completely determined by GC analyses.

**Biphenyl (2a)**: White solid, m.p. 68—71 °C (uncorrected) (lit.<sup>10</sup> m.p. 69—70 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.59 (d, *J*=8.4 Hz, 4H), 7.44 (t, *J*=8.0 Hz, 4H), 7.39 (t, *J*=7.6 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 141.2, 129.9, 128.7, 127.2; MS *m/z* (%): 154 (M<sup>+</sup>, 100), 76 (40).

**4,4'-Dimethyl-biphenyl (2b)**: White solid, m.p. 117—121 °C (uncorrected) (lit.<sup>11</sup> m.p. 122—123 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.46 (d, *J*=8.0 Hz, 4H), 7.22 (d, *J*=7.6 Hz, 4H), 2.37 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 138.3, 136.7, 129.4, 126.8, 21.0; MS *m/z* (%): 182 (M<sup>+</sup>, 100), 164 (75), 92 (100), 77 (7).

**2,2'-Dimethyl-biphenyl (2c)**: Colorless oil.<sup>6c,7a</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.25—7.20 (m, 6H), 7.09 (d, *J*=7.6 Hz, 2H), 2.04 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 141.6, 135.8, 129.8, 129.3, 127.1, 125.5, 19.8; MS *m/z* (%): 182 (M<sup>+</sup>, 100), 164 (53), 92 (40), 75 (13).

**4,4'-Dimethoxy-biphenyl (2d)**: White solid, m.p. 175—179 °C (uncorrected) (lit.<sup>11</sup> m.p. 176—177 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.46 (d, *J*=8.8 Hz, 4H), 7.22 (d, *J*=8.8 Hz, 4H), 3.82 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 138.3, 136.7, 129.4, 126.8, 55.3; MS *m/z* (%): 214 (M<sup>+</sup>, 100), 200 (31), 183 (100), 76 (11).

**1,1'-Binaphyl (2e)**: White solid, m.p. 143—146 °C (uncorrected) (lit.<sup>6,7</sup> m.p. 144—145 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.86—7.83 (m, 7H), 7.49—7.46 (m, 7H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 133.4, 127.9, 125.8, 125.4; MS *m/z* (%): 254 (M<sup>+</sup>, 100), 127 (57).

**N<sup>4</sup>,N<sup>4</sup>,N<sup>4</sup>,N<sup>4</sup>-Tetramethyl-biphenyl-4,4'-diamine (2f)**: White solid, m.p. 192—195 °C (uncorrected) (lit.<sup>12</sup> m.p. 193—194 °C). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.05 (d, *J*=8.0 Hz, 4H), 6.63 (d, *J*=8.0 Hz, 4H), 2.94 (s, 12H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 129.7, 113.4, 41.3, 40.2; MS *m/z* (%): 240 (M<sup>+</sup>, 100), 226 (23), 196 (45), 77 (8).

**1,1'-Binaphthyl-2,2'-diol (2j)**: White solid, m.p. 213—217 °C (uncorrected) (lit.<sup>13</sup> m.p. 215 °C). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.98 (d, *J*=9.0 Hz, 2H), 7.89 (d, *J*=8.7 Hz, 2H), 7.40—7.26 (m, 6H), 7.15 (d, *J*=6.6 Hz, 2H), 1.54 (s, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 153.1, 133.7, 131.8, 129.8, 128.8, 124.5, 124.4, 118.1, 111.2; MS *m/z* (%): 286 (M<sup>+</sup>, 100), 268 (83), 142 (25).

**2,6,2',6'-Tetramethoxy-biphenyl (2k)**: White solid, m.p. 173—174 °C (uncorrected) (lit.<sup>14</sup> m.p. 174—175 °C). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 6.93—6.83 (m, 6H), 3.79 (s, 6H), 3.72 (s, 6H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 153.7, 151.7, 129.0, 117.5, 113.8, 112.9, 56.9, 56.1; MS *m/z* (%): 274 (M<sup>+</sup>, 100), 244 (51), 74 (7).

**Biphenyl-3,3'-dicarboxylic acid diethyl ester (2n)**: White solid, m.p. 158—162 °C (uncorrected) (lit.<sup>6,7</sup> m.p. 159—160 °C). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 8.30 (s, 2H), 8.05 (d, *J*=7.8 Hz, 2H), 7.82 (d, *J*=6.9 Hz, 2H), 7.56 (t, *J*=8.0 Hz, 2H), 4.46—4.39 (m, 4H), 1.43 (t, *J*=7.2 Hz, 6H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ:

166.8, 140.8, 131.8, 131.5, 129.3, 129.1, 128.6, 61.5, 14.7; MS *m/z* (%): 298 (M<sup>+</sup>, 100), 254 (23), 225 (40), 75 (9).

## References

- (a) Jia, L.-Q.; Jiang, H.-F.; Li, J.-H. *Chem. Commun.* **1999**, 985.  
(b) Li, J.-H.; Jiang, H.-F. *Chem. Commun.* **1999**, 2369.  
(c) Li, J.-H.; Jiang, H.-F.; Chen, M.-C. *Green Chem.* **2001**, 3, 137.  
(d) Li, J.-H.; Jiang, H.-F.; Chen, M.-C. *Chin. J. Chem.* **2001**, 19, 1153.  
(e) Li, J.-H.; Xie, Y.-X.; Yin, D.-L.; Jiang, H.-F. *Green Chem.* **2002**, 4, 424.  
(f) Li, J.-H.; Xie, Y.-X.; Yin, D.-L.; Jiang, H.-F. *Chin. J. Chem.* **2003**, 21, 714 and references cited therein.  
(g) Brown, R. A.; Pollet, P.; Mckoon, E.; Eckert, C. A.; Liotta, C. L.; Jessop, P. G. *J. Am. Chem. Soc.* **2001**, 123, 1254.
- For representative reviews, see:  
(a) Jessop, P. G. and Leitner, W., *Chemical Synthesis Using Supercritical Fluids*, Wiley-VCH, Weinheim, **1999**.  
(b) Jessop, P. G.; Ikariya, T.; Noyori, R. *Chem. Rev.* **1999**, 99, 475.  
(c) Li, J.; Jia, L.; Jiang, H. *Chin. J. Org. Chem.* **2000**, 20, 293 (in Chinese).  
(d) Oakes, R. S.; Clifford, A. A.; Rayner, C. M. *J. Chem. Soc., Perkin Trans. 1* **2001**, 917.
- (a) Bringmann, G.; Walter, R.; Weirich, R. *Angew. Chem., Int. Ed. Engl.* **1990**, 29, 977.  
(b) Zhang, S.; Zhang, D.; Liebeskind, L. S. *J. Org. Chem.* **1997**, 62, 2312 and references cited therein.
- For Ni catalyzed Ullmann-type couplings, see:  
(a) Takagi, K.; Hayama, N.; Sasaki, K. *Bull. Chem. Soc. Jpn.* **1984**, 57, 1887.  
(b) Meyer, G.; Rollin, Y.; Perichon, J. *J. Organomet. Chem.* **1987**, 333, 263.
- For Pd/C catalyzed Ullmann-type couplings using Zn and water as the reducing reagent, see:  
(a) Ventrakaman, S.; Li, C. *J. Org. Lett.* **1999**, 1133.  
(b) Ventrakaman, S.; Li, C. *Tetrahedron Lett.* **2000**, 41, 4831 and references cited therein.  
(c) Mukhopadhyay, S.; Rothenberg, G.; Gitis, D.; Sasson, Y. *J. Org. Lett.* **2000**, 211.  
(d) Li, J.-H.; Xie, Y.-X.; Yin, D.-L. *J. Org. Chem.* **2003**, 68, 9867.
- For Pd/C catalyzed Ullmann-type couplings using other reducing reagents, see:  
(I) Formate salts as the reducing reagent:  
(a) Mukhopadhyay, S.; Rothenberg, G.; Gitis, D.; Wiener, H.; Sasson, Y. *J. Chem. Soc., Perkin Trans. 2* **1999**, 2481.  
(b) Mukhopadhyay, S.; Rothenberg, G.; Qafisheh, N.; Sasson, Y. *Tetrahedron Lett.* **2001**, 42, 6117.  
(II) Hydrogen gas as the reducing reagent:  
(c) Mukhopadhyay, S.; Rothenberg, G.; Wiener, H.; Sasson, Y. *Tetrahedron* **1999**, 55, 14763 and references cited therein.
- For other Pd-catalyzed reductive Ullmann-type couplings, see:  
(a) Kuroboshi, M.; Waki, Y.; Tanaka, H. *J. Org. Chem.* **2003**,

- 68, 3938 and references cited therein.
- (b) Hassan, J.; Hathroubi, C.; Gozzi, C.; Lamaire, M. *Tetrahedron* **2001**, 57, 7845.
- (c) Hassan, J.; Penalva, V.; Lavenot, L.; Gozzi, C.; Lemaire, M. *Tetrahedron* **1998**, 54, 13793.
- (d) Penalva, V.; Hassan, J.; Lavenot, L.; Gozzi, C.; Lemaire, M. *Tetrahedron Lett.* **1998**, 39, 2559.
- (e) Hennings, D. D.; Iwama, T.; Rawel, V. H. *Org. Lett.* **1999**, 1, 1205.
- 8 (a) Bamfield, P.; Quan, P. M. *Synthesis* **1978**, 537.
- (b) Hassan, J.; Penalva, V.; Lavenot, L.; Gozzi, C.; Lemaire, M. *Tetrahedron* **1998**, 54, 13793.
- 9 (a) Peyrot F.; Martin, M.-T.; Migault, J.; Ducrocq, C. *Eur. J. Org. Chem.* **2003**, 172.
- (b) Li, J.-H.; Xie, Y.-X.; Yin, D.-L. *Green Chem.* **2002**, 4, 505.
- (c) Gabriele, B.; Salerno, G.; Costa, M.; Chiusoli, G. P. *Chem. Commun.* **1999**, 1381 and references cited therein.
- 10 Penso, M.; Albanese, D.; Landini, D.; Lupi, V. *J. Mol. Catal. A: Chem.* **2003**, 204–205, 177.
- 11 Tamura, Y.; Chun, M. W.; Inoue, K.; Minamikawa, J. *Synthesis* **1978**, 822.
- 12 Morkovnik, A. S. *Zhur. Obsh. Khim.* **1989**, 59, 921.
- 13 Nassimbeni, L. R. *J. Chem. Soc., Perkin Trans. 2* **2002**, 1246.
- 14 Goeran, L. *J. Org. Chem.* **1987**, 52, 547.

(E0403292 ZHAO, X. J.)