Cross-Coupling

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Convenient and General Palladium-Catalyzed Carbonylative Sonogashira Coupling of Aryl Amines**

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Alkynones represent an interesting structural motif that is found in various bioactive molecules.[1] More importantly, they constitute key intermediates for the synthesis of numerous natural products,[2] especially heterocycles.[3] In general, alkynones have been prepared by the reaction of acid chlorides and alkynes. Unfortunately, this methodology is limited with respect to functional group tolerance and substrate stability.[4]

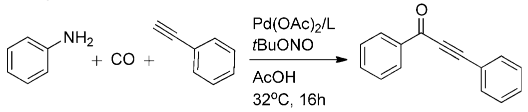
Since the first report by Kobayashi and Tanaka in 1981,[5a] notable improvements of palladium-catalyzed carbonylative Sonogashira reactions of aryl halides have been achieved.[5,6] A drawback to all these elegant developments is the necessity to use iodo compounds as substrates. Hence, our development of a general procedure for carbonylative Sonogashira reactions of less expensive aryl bromides is interesting.[6a] Key to the success was the application of a palladium/$BuPAd_2$ catalyst system[7] in the presence of potassium carbonate as base. In addition to aryl halides, carbonyaltive Sonogashira coupling reactions of aryl triflates are also achieved.[6b] The latter procedure opened the gate for using hydroxylated arenes, which are frequently found in pharmaceuticals, agrochemicals, and natural products, as starting materials.[8]

Aryl amines are abundantly available and relatively inexpensive. Compared to aryl halides, they have been scarcely employed as electrophiles in palladium-catalyzed coupling methodologies. However, they can be easily activated by simple diazotization under mild reaction conditions.[9] Notably, the first carbonylation of isolated diazonium salts was reported by Matsuda and co-workers.[10] Since then, all other examples of such carbonylation processes required isolated ArN_2BF_4 salts as coupling partners.[11] Given their commercial availability, the hazards they pose, and their tedious preparation, it would be interesting to develop processes that can employ anilines directly as electrophiles.

Based on our continuing interest in carbonylations of aryl−X derivatives,[12,13] and considering the importance of alkynones,[1–3] herein we report the palladium-catalyzed coupling of in situ formed arenediazonium salts with carbon monoxide and alkynes under mild reaction conditions. To the best of our knowledge such carbonylative Sonogashira coupling reactions of diazonium salts are not known to date.[14]

The first set of reactions was carried out using aniline and phenylacetylene as a model system at ambient conditions (32 °C). In the presence of 2 mol% $Pd(OAc)_2$ and 6 mol% TFP, different solvents were tested (Table 1, entries 1–6). DMSO and DMF gave 43% and 38%, respectively, of the desired product 1,3-diphenylprop-2-yn-1-one (Table 1, entries 1–2), whereas 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (DMPU) only resulted in 10% of the product (Table 1, entry 3). Similarly, toluene gave 10% yield (Table 1, entry 6). In contrast, 48% of the desired product is achieved in THF (Table 1, entry 4). Thus, we choose THF to investigate the effect of different ligands: In the absence of a ligand only a low yield (12%) is observed (Table 1, entry 7). Surprisingly, the standard ligand, PPh_3, inhibited this carbonylative coupling and gave only 2% of the corresponding product (Table 1, entry 8). In the same way, bidentate phosphine

Table 1: Palladium-catalyzed carbonylative sonogashira coupling of anilines: Optimization of reaction conditions.[a]



Entry	Ligand	Solvent	Yield [%][b]
1	TFP (6 mol%)	DMSO (2 mL)	43
2	TFP (6 mol%)	DMF (2 mL)	38
3	TFP (6 mol%)	DMPU (2 mL)	10
4	TFP (6 mol%)	THF (2 mL)	48
5	TFP (6 mol%)	1,4-dioxane (2 mL)	31
6	TFP (6 mol%)	toluene (2 mL)	10
7	–	THF (2 mL)	12
8	PPh_3 (6 mol%)	THF (2 mL)	2
9	P(*o*-tolyl)$_3$ (6 mol%)	THF (2 mL)	23
10	Xantphos (3 mol%)	THF (2 mL)	<1
11	DPEphos (3 mol%)	THF (2 mL)	<1
12	DPPP (3 mol%)	THF (2 mL)	<1
13	TFP (6 mol%)	THF (1 mL) DMSO (1 mL)	60
14	**TFP (6 mol%)**	**THF (1 mL)** **DMSO (1 mL)**	**81[c]**
15	TFP (6 mol%)	THF (1 mL) DMSO (1 mL)	55[c,d]

[a] Reaction conditions: aniline (1.3 mmol), *t*BuONO (1.3 mmol), AcOH (1.3 mmol), phenylacetylene (1 mmol), $Pd(OAc)_2$ (2 mol%), CO (10 bar), 32 °C, 16 h. [b] Determined by GC analysis of the reaction mixture using hexadecane as an internal standard. Based on phenylacetylene. [c] Aniline (2 mmol), *t*BuONO (2 mmol), AcOH (2 mmol). [d] CO (1 bar). DPEphos = (oxydi-2,1-phenylene)bis(diphenylphosphine), DPPP = 1,3-bis(diphenylphosphino)propane, P(*o*-tolyl)$_3$ = tri(*o*-tolyl)phosphine, TFP = tri(2-furyl)phosphine, Xantphos = 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene.

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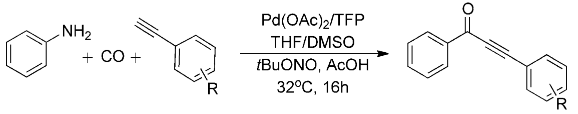
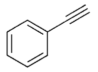
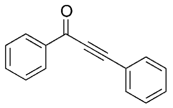
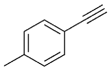
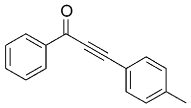
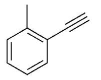
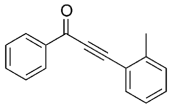
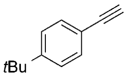
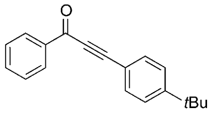
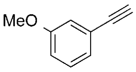
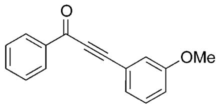
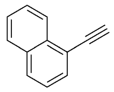
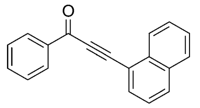
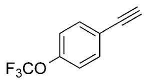
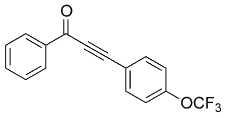
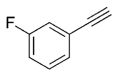
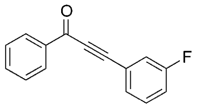
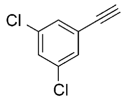
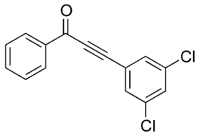
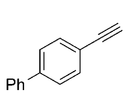
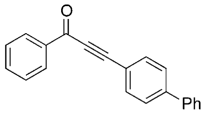
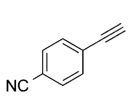
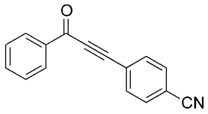
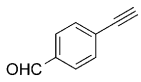
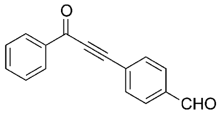
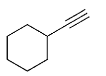
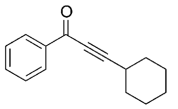
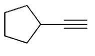
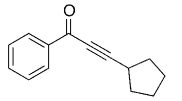
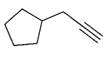
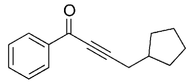
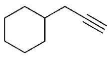
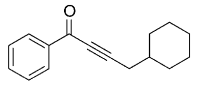
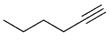
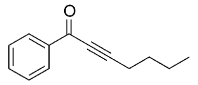
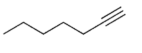
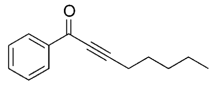
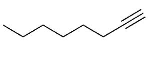
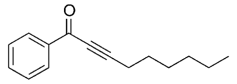
Table 2: Palladium-catalyzed carbonylative Sonogashira coupling of anilines: Variation of alkynes.[a]



Entry	Alkyne	Product	Yield [%][b]
1			81
2			80
3			75
4			69
5			59
6			86
7			65
8			90
9			88
10			93
11			81
12			75
13			91
14			68
15			89
16			92
17			80
18			83
19			85

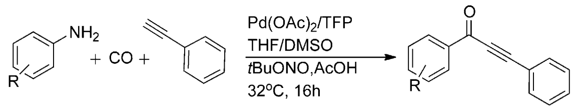
[a] Reaction conditions: aniline (2 mmol), *t*BuONO (2 mmol), AcOH (2 mmol), alkynes (1 mmol), CO (10 bar), $Pd(OAc)_2$ (2 mol%), TFP (6 mol%), THF (1 mL), DMSO (1 mL), 32 °C, 16 h. [b] Determined by GC analysis of the reaction mixture using hexadecane as an internal standard. Based on alkyne; average of two runs.

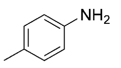
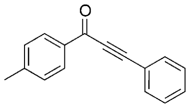
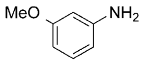
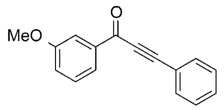
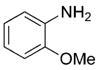
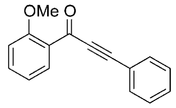
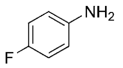
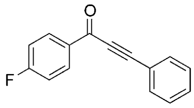
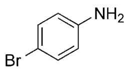
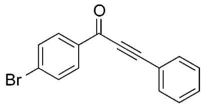
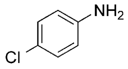
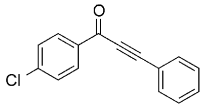
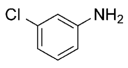
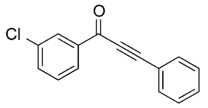
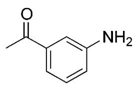
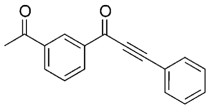
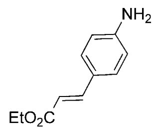
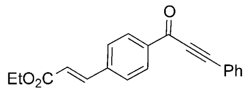
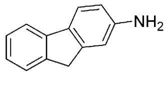
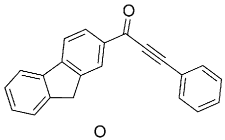
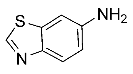
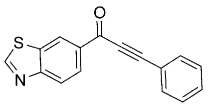
ligands were not suitable and gave trace amounts of the alkynone together with the homocoupling product of phenylacetylene (Table 1, entries 10–12). To our delight, a 60% product yield is obtained by using a mixture of THF and DMSO ($v/v = 1{:}1$) as the solvent (Table 1, entry 13). The yield is further improved to 81% by increasing the amount of aniline (Table 1, entry 14). Although most reactions were carried out at 10 bar of CO, notably, the reaction can be performed without pressure to give 55% of the carbonylation product (Table 1, entry 15). With the best reaction conditions in hand, we examined different substrates for this novel carbonylative Sonogashira reaction. The generality of this methodology is demonstrated by the results in Tables 2 and 3.

Simple alkyl- and methoxy-substituted aromatic alkynes are successfully coupled with CO and give good yields of the corresponding products (Table 2, entries 2–6). Besides electron-donating groups, electron-withdrawing substituents are tolerated and lead to good yields (Table 2, entries 7–12). Notably, aldehydes might be potentially oxidized by *t*BuONO; however, to our surprise 75% of the corresponding alkynone is produced (Table 2, entry 12). Furthermore seven different aliphatic alkynes were transformed into the desired alkynones in excellent yields (Table 2, entries 13–19). Compared with aromatic alkynes, aliphatic alkynes are more selective, and only trace amounts of the noncarbonylation products were formed.

As demonstrated in Table 3 eleven different anilines were tested to prove the generality of this methodology. Not only electron-donating (Table 3, entries 1–3), but also electron-withdrawing groups attached to the aniline are well tolerated (Table 3, entries 4–9). Heterocyclic amines can also be used as

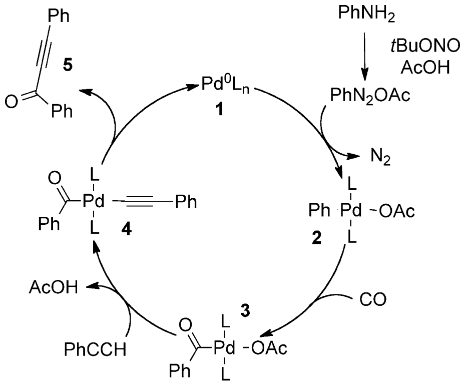
Table 3: Palladium-catalyzed carbonylative Sonogashira coupling of anilines: Variation of anilines.[a]



Entry	Aniline	Product	Yield [%][b]
1			75
2			82
3			79
4			83
5			81
6			75
7			68
8			88
9			62
10			60
11			55

[a] Reaction conditions: aniline (2 mmol), *t*BuONO (2 mmol), AcOH (2 mmol), phenylacetylene (1 mmol), CO (10 bar), $Pd(OAc)_2$ (2 mol%), TFP (6 mol%), THF (1 mL), DMSO (1 mL), 32 °C, 16 h. [b] Determined by GC analysis of the reaction mixture using hexadecane as an internal standard. Based on phenylacetylene; average of two runs.

starting materials and 6-aminobenzothiazole resulted in 55 % of the desired product (Table 3, entry 11).



Scheme 1. Proposed reaction mechanism.

In Scheme 1 the proposed reaction mechanism of this diazotization/carbonylative coupling sequence is depicted. Initially, diazotization of the aniline takes place. Then, oxidative addition of the resulting diazonium salt to Pd^0 (**1**), which is generated from $Pd(OAc)_2$, with subsequent coordination to give **2** and then insertion of carbon monoxide forms the acyl palladium complex **3**. Under the assistance of acetate, phenylacetylene is deprotonated and generates **4** which gives the terminal product **5** after reductive elimination, and also regenerates the active Pd^0 species for next catalytic cycle.

In conclusion, the first general and efficient methodology for carbonylative Sonogashira reactions of anilines has been developed. The transformation proceeds under mild reaction conditions, and no base is needed. Both aromatic and aliphatic alkynes are suitable starting materials and 30 different kinds of alkynones were produced in moderate to excellent yields.

Experimental Section

General comments: All reactions were prepared under argon atmosphere. DMSO and THF were distilled from sodium ketyl or CaH and stored in Aldrich Sure/Stor flasks under argon. $Pd(OAc)_2$, anilines, alkynes, AcOH, *tert*-BuONO and all the ligands were purchased from Aldrich and used as received. Gas chromatography analysis was performed on an Agilent HP-5890 instrument with a FID detector and HP-5 capillary column (polydimethylsiloxane with 5 % phenyl groups, 30 m, 0.32 mm i.d., 0.25 μm film thickness) using argon as carrier gas. Gas chromatography/mass analysis was carried out on an Agilent HP-5890 instrument with an Agilent HP-5973 Mass Selective Detector (EI) and HP-5 capillary column (polydimethylsiloxane with 5 % phenyl groups, 30 m, 0.25 mm i.d., 0.25 μm film thickness) using helium carrier gas.

Typical reaction procedure for carbonylative Sonogashira reactions: $Pd(OAc)_2$ (2 mol %) and TFP (6 mol %) were transferred into a vial (4 mL reaction volume) equipped with a septum, a small cannula, and a stirring bar. After the vial was purged with argon, DMSO (1 mL), THF (1 mL), aniline (2.0 mmol), *tert*-butyl nitrite (2.0 mmol), AcOH (2.0 mmol), and phenylacetylene (1 mmol) were injected into the vial by syringe. Then, the vial was placed on an alloy plate, which was transferred into a 300 mL autoclave of the 4560 series from Parr Instruments under argon atmosphere. After flushing the autoclave three times with CO, a pressure of 10 bar was set and the reaction was performed for 16 h at 32 °C. After the reaction was complete, the autoclave was cooled to room temperature and the pressure was released carefully. Hexadecane (0.1 mmol) was added to the reaction mixture and a portion of the mixture was taken for GC and GC/MS analysis after proper mixing. For isolation the reaction mixture was partitioned between ethyl acetate and saturated NH_4Cl. The combined organic layers were washed with brine and dried afterwards with magnesium sulphate. After column chromatography on silica gel (heptane/ethyl acetate 40:1) the desired products were isolated in pure form.

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[1] a) C. H. Faweett, R. D. Firu, D. M. Spencer, *Physiol. Plant Pathol.* **1971**, *1*, 163 – 166; b) K. Imai, *J. Pharm. Soc. Jpn.* **1956**, *76*, 405 – 408; c) C. A. Quesnelle, P. Gill, M. Dodier, D. St. Laurent, M. Serrano-Wu, A. Marinier, A. Martel, C. E. Mazzucco, T. M. Stickle, J. F. Barrett, D. M. Vyas, B. N. Balasubramanian, *Bioorg. Med. Chem. Lett.* **2003**, *13*, 519 – 524.

[2] a) A. S. Karpov, E. Merkul, F. Rominger, T. J. J. Müller, *Angew. Chem.* **2005**, *117*, 7112 – 7117; *Angew. Chem. Int. Ed.* **2005**, *44*, 6951 – 6956; b) D. M. D'Souza, T. J. J. Müller, *Nat. Protoc.* **2008**, *3*, 1660 – 1665; c) J. Marco-Contelles, E. de Opazo, *J. Org. Chem.* **2002**, *67*, 3705 – 3717; d) C. J. Forsyth, J. Xu, S. T. Nguyen, I. A. Samdai, L. R. Briggs, T. Rundberget, M. Sandvik, C. O. Miles, *J. Am. Chem. Soc.* **2006**, *128*, 15114 – 15116; e) L. F. Tietze, R. R. Singidi, K. M. Gericke, H. Bockemeier, H. Laatsch, *Eur. J. Org. Chem.* **2007**, 5875 – 5878.

[3] a) B. Willy, T. J. J. Müller, *Arkivoc* **2008**, 195 – 208; b) A. Arcadi, M. Aschi, F. Marinelli, M. Verdecchia, *Tetrahedron* **2008**, *64*, 5354 – 5361; c) P. Bannwarth, A. Valleix, D. Gree, R. Gree, *J. Org. Chem.* **2009**, *74*, 4646 – 4649.

[4] a) K. Y. Lee, M. J. Lee, J. N. Kim, *Tetrahedron* **2005**, *61*, 8705 – 8710; b) H. A. Stefani, R. Cella, F. A. Dorr, C. M. P. de Pereira, F. P. Gomes, G. Zeni, *Tetrahedron Lett.* **2005**, *46*, 2001 – 2003; c) S. S. Palimkar, P. H. Kumar, N. R. Jogdand, T. Daniel, R. J. Lahoti, K. V. Srinivasan, *Tetrahedron Lett.* **2006**, *47*, 5527 – 5530; d) S. J. Yim, C. H. Kwon, D. K. An, *Tetrahedron Lett.* **2007**, *48*, 5393 – 5395; e) M. M. Jackson, C. Leverett, J. F. Toczko, J. C. Roberts, *J. Org. Chem.* **2002**, *67*, 5032 – 5035; f) D. A. Alonso, C. Nájera, M. C. Pacheco, *J. Org. Chem.* **2004**, *69*, 1615 – 1619; g) B. Wang, M. Bonin, L. Micouin, *J. Org. Chem.* **2005**, *70*, 6126 – 6128; h) L. Chen, C. Li, *Org. Lett.* **2004**, *6*, 3151 – 3153; i) N. Kakusawa, K. Yamaguchi, J. Kurita, T. Tsuchiya, *Tetrahedron Lett.* **2000**, *41*, 4143 – 4146.

[5] a) T. Kobayashi, M. Tanaka, *J. Chem. Soc. Chem. Commun.* **1981**, 333 – 334; b) J. Liu, X. Peng, W. Sun, Y. Zhao, C. Xia, *Org. Lett.* **2008**, *10*, 3933 – 3936; c) M. S. Mohamed Ahmed, A. Mori, *Org. Lett.* **2003**, *5*, 3057 – 3060; d) J. Liu, J. Chen, C. Xia, *J. Catal.* **2008**, *253*, 50 – 56; e) S. Kang, K. Lim, P. Ho, W. Kim, *Synthesis* **1997**, 874 – 876; f) L. Delaude, A. M. Masdeu, H. Alper, *Synthesis* **1994**, 1149 – 1151; g) A. Arcadi, S. Cacchi, F. Marinelli, P. Pace, G. Sanzi, *Synlett* **1995**, 823 – 824; h) M. Iizuka, Y, Kondo, *Eur. J. Org. Chem.* **2007**, 5180 – 5182; i) V. Sans, A. M. Trzeciak, S. Luis, J. J. Ziólkowski, *Catal. Lett.* **2006**, *109*, 37 – 41; j) T. Fukuyama, R. Yamaura, I. Ryu, *Can. J. Chem.* **2005**, *83*, 711 – 715; k) M. T. Rahman, T. Fukuyama, N. Kamata, M. Sato, I. Ryu, *Chem. Commun.* **2006**, 2236 – 2238; l) B. Liang, M. Huang, Z. You, Z. Xiong, K. Lu, R. Fathi, J. Chen, Z. Yang, *J. Org. Chem.* **2005**, *70*, 6097 – 6100; m) A. Fusano, T. Fukuyama, S. Nishitani, T. Inouye, I. Ryu, *Org. Lett.* **2010**, *12*, 2410 – 2413; n) A. Park, K. Park, Y. Kim, S. Lee, *Org. Lett.* **2011**, *13*, 944 – 947; o) P. J. Tambade, Y. P. Patil, N. S. Nandurkar, B. M. Bhanage, *Synlett* **2008**, 886 – 888.

[6] a) X. F. Wu, H. Neumann, M. Beller, *Chem. Eur. J.* **2010**, *16*, 12104 – 12107; b) X. F. Wu, B. Sundararaju, H. Neumann, P. H. Dixneuf, M. Beller, *Chem. Eur. J.* **2011**, *17*, 106 – 110.

[7] For some other applications of this catalyst system, see: a) S. Klaus, H. Neumann, A. Zapf, D. Strübing, S. Hübner, J. Almena, T. Riermeier, P. Groß, M. Sarich, W.-R. Krähnert, K. Rossen, M. Beller, *Angew. Chem.* **2006**, *118*, 161 – 165; *Angew. Chem. Int. Ed.* **2006**, *45*, 154 – 158; b) A. Brennführer, H. Neumann, S. Klaus, T. Riermeier, J. Almena, M. Beller, *Tetrahedron* **2007**, *63*, 6252 – 6258; c) A. G. Sergeev, A. Zapf, A. Spannenberg, M. Beller, *Organometallics* **2008**, *27*, 297 – 300; d) H. Neumann, A. Brennführer, P. Groß, T. Riermeier, J. Almena, M. Beller, *Adv. Synth. Catal.* **2006**, *348*, 1255 – 1261; e) H. Neumann, A. Brennführer, M. Beller, *Chem. Eur. J.* **2008**, *14*, 3645 – 3652; f) A. Tewari, M. Hein, A. Zapf, M. Beller, *Tetrahedron* **2005**, *61*, 9705 – 9709: g) A. Ehrentraut, A. Zapf, M. Beller, *Synlett* **2000**, 1589 – 1592; h) A. Zapf, A. Ehrentraut, M. Beller, *Angew. Chem.* **2000**, *112*, 4315 – 4317; *Angew. Chem. Int. Ed.* **2000**, *39*, 4153 – 4155; i) A. Tewari, M. Hein, A. Zapf, M. Beller, *Synthesis* **2004**, 935 – 941; j) A. Köllhofer, T. Pullmann, H. Plenio, *Angew. Chem.* **2003**, *115*, 1086 – 1088; *Angew. Chem. Int. Ed.* **2003**, *42*, 1056 – 1058; k) A. Ehrentraut, A. Zapf, M. Beller, *Adv. Synth. Catal.* **2002**, *344*, 209 – 217; l) A. G. Sergeev, A. Spannenberg, M. Beller, *J. Am. Chem. Soc.* **2008**, *130*, 15549 – 15563.

[8] a) J. H. P. Tyman, *Synthetic and Natural Phenols*, Elsevier, New York, **1996**; b) Z. Rappoport, *The Chemistry of Phenols*, Wiley-VCH, Weinheim, **2003**; c) J. F. Hartwig in *Handbook of Organopalladium Chemistry for Organic Synthesis*, *Vol. 1* (Ed.: E.-I. Negishi), Wiley-Interscience, New York, **2002**, p. 1097.

[9] For reviews using diazonium salts as coupling partners, see: a) A. Roglans, A. Pla-Quintana, M. Moreno-Mañas, *Chem. Rev.* **2006**, *106*, 4622 – 4643; b) J. G. Taylor, A. V. Moro, C. R. D. C. Correia, *Eur. J. Org. Chem.* **2011**, 1403 – 1428; c) F. X. Felpin, L. Nassar-Hardy, F. Le Callonnec, E. Fouquet, *Tetrahedron* **2011**, *67*, 2815 – 2831; for recent examples, see: d) F. Le Callonnec, E. Fouquet, F. X. Felpin, *Org. Lett.* **2011**, *13*, 2646 – 2649; e) B. Schmidt, F. Hölter, R. Berger, S. Jessel, *Adv. Synth. Catal.* **2010**, *352*, 2463 – 2473.

[10] a) K. Nagira, K. Kikukawa, F. Wada, T. Matsuda, *J. Org. Chem.* **1980**, *45*, 2365 – 2368; b) K. Kikukawa, K. Kono, K. Nagira, F. Wada, T. Matsuda, *J. Org. Chem.* **1981**, *46*, 4413 – 4416; c) K. Kikukawa, K. Kono, K. Nagira, F. Wada, T. Matsuda, *Tetrahedron Lett.* **1980**, *21*, 2877 – 2878.

[11] For some other samples on carbonylative coupling of diazonium salts, see: a) U. Siegrist, T. Rapold, H. Blaser, *Org. Process Res. Dev.* **2003**, *7*, 429 – 431; b) S. Sengupta, S. K. Sadhukhan, S. Bhattacharyya, J. Guha, *J. Chem. Soc. Perkin Trans. 1* **1998**, 407 – 410; c) R. J. Herr, D. J. Fairfax, H. Meckler, J. D. Wilson, *Org. Process Res. Dev.* **2002**, *6*, 677 – 681; d) M. B. Andrus, Y. Ma, Y. Zang, C. Song, *Tetrahedron Lett.* **2002**, *43*, 9137 – 9140; e) Y. Ma, C. Song, Q. Chai, C. Ma, M. B. Andrus, *Synthesis* **2003**, 2886 – 2889; f) X. F. Wu, J. Schranck, H. Neumann, M. Beller, *Tetrahedron Lett.* **2011**, *52*, 3702 – 3704.

[12] For reviews on palladium-catalyzed carbonylations, see: a) A. Brennführer, H. Neumann, M. Beller, *Angew. Chem.* **2009**, *121*, 4176 – 4196; *Angew. Chem. Int. Ed.* **2009**, *48*, 4114 – 4133; b) A. Brennführer, H. Neumann, M. Beller, *ChemCatChem* **2009**, *1*, 28 – 41; c) "Carbonylation of Benzyl- and Aryl-X Compounds": M. Beller in *Applied Homogeneous Catalysis with Organometallic Compounds*, 2nd ed. (Eds.: W. A. Herrmann, B. Cornils), Wiley-VCH, Weinheim, **2002**, pp. 145 – 156; d) R. Skoda-Foldes, L. Kollár, *Curr. Org. Chem.* **2002**, *6*, 1097 – 1119; e) M. Beller, B. Cornils, C. D. Frohning, C. W. Kohlpaintner, *J. Mol. Catal. A* **1995**, *104*, 17 – 85; f) R. Grigg, S. P. Mutton, *Tetrahedron* **2010**, *66*, 5515 – 5548.

[13] a) X. F. Wu, H. Neumann, M. Beller, *Adv. Synth. Catal.* **2011**, *353*, 788 – 792; b) X. F. Wu, H. Neumann, M. Beller, *Angew. Chem.* **2010**, *122*, 5412 – 5416; *Angew. Chem. Int. Ed.* **2010**, *49*, 5284 – 5288; c) X. F. Wu, P. Anbarasan, H. Neumann, M. Beller, *Angew. Chem.* **2010**, *122*, 7474 – 7477; *Angew. Chem. Int. Ed.*

2010, *49*, 7316–7319; d) X. F. Wu, H. Neumann, M. Beller, *Chem. Asian J.* **2010**, *5*, 2168–2172; e) X. F. Wu, H. Neumann, M. Beller, *ChemCatChem* **2010**, *2*, 509–513; f) X. F. Wu, H. Neumann, M. Beller, *Chem. Eur. J.* **2010**, *16*, 9750–9753; g) X. F. Wu, H. Neumann, M. Beller, *Tetrahedron Lett.* **2010**, *51*, 6146–6149; h) X. F. Wu, H. Neumann, A. Spannenberg, T. Schulz, H. Jiao, M. Beller, *J. Am. Chem. Soc.* **2010**, *132*, 14596–14602; i) X.-F. Wu, H. Jiao, H. Neumann, M. Beller, *ChemCatChem* **2011**, *3*, 726–733; j) X. F. Wu, B. Sundararaju, P. Anbarasan, H. Neumann, P. H. Dixneuf, M. Beller, *Chem. Eur. J.* **2011**, *17*, 8014–8017.

[14] For examples to use diazonium salts in noncarbonylative Sonogashira couplings, see: a) S. Darses, G. Michaud, J. P. Genêt, *Eur. J. Org. Chem.* **1999**, 1875–1883; b) G. Fabrizi, A. Goggiamani, A. Sferrazza, S. Cacchi, *Angew. Chem.* **2010**, *122*, 4161–4164; *Angew. Chem. Int. Ed.* **2010**, *49*, 4067–4070; c) B. Panda, T. K. Sarkar, *Chem. Commun.* **2010**, *46*, 3131–3133; d) X. F. Wu, H. Neumann, M. Beller, *Chem. Commun.* **2011**, *47*, 7959–7961.