DOI: 10.1002/adsc.201700307
Advanced Synthesis & Catalysis

Diethyloxalate as "CO" Source for Palladium-Catalyzed Ethoxycarbonylation of Bromo- and Chloroarene Derivatives

Amandine Monrose,[a] Helori Salembier,[a] Till Bousquet,[a] Sylvain Pellegrini,[a,*] and Lydie Pélinski[a,*]

[a] University of Lille, CNRS, ENSCL, Centrale Lille, Univ. Artois,UMR 8181 – UCCS – Unité de Catalyse et Chimie du Solide, F-59000 Lille, France
Fax: (+33) 3 20 43 65 85; e-mail: sylvain.pellegrini@univ-lille1.fr; lydie.pelinski@univ-lille1.fr

Received: May 13, 2017; Revised: May 3, 2017; Published online: ■■ ■■, 0000

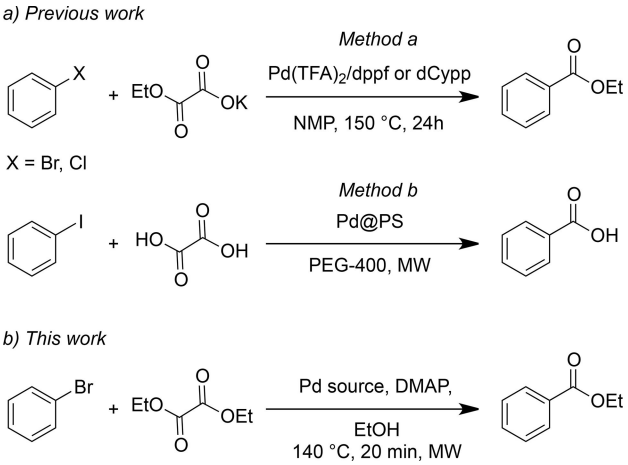
Supporting information for this article is available on the WWW under https://doi.org/10.1002/adsc.201700307

Abstract: Palladium(II)-catalyzed ethoxycarbonylation of aryl bromides with diethyloxalate oxalate is described. Functionalized aromatic esters can be efficiently synthesized with only 0.65 mol % $PdCl_2(PPh_3)_2$ catalyst under microwave irradiation and without additional ligand. This method illustrates an inexpensive and operationally simple method for the preparation of aromatic esters.

Keywords: Esterification; carbonylation; diethyloxalate; palladium

Carboxylic esters are found in many natural products and pharmaceutical compounds. Regarding their importance, palladium-catalyzed carbonylation reactions of aromatic halides employing CO and CO_2 have been investigated extensively for the synthesis of acids and their derivatives such as esters and amides.[1] However, the use of highly active CO gas is restricted due to its toxicity and high pressure reaction conditions. For this reason, the development of alternative ways to produce CO in the reaction mixture is of considerable interest in synthetic organic chemistry.[2] In this context, carbonylation involving in situ generation of CO from surrogates such as $Mo(CO)_6$,[3] aldehydes,[4] silacarboxylic acids,[5] formates,[6] formic acid[7] and alcohols[8] was developed. More recently, a carbonylative esterification reaction between aryl bromides and alcohols in the presence of oxiranes as CO source has been reported.[9]

At the same time, Gooßen and co-workers discovered that the Pd/Cu-catalyzed decarboxylative cross-coupling of α-oxocarboxylates gave rise to ketones.[10] This method has been applied to realize ortho-acylation of acetanilides and C2-acylation of indoles.[11] Inspired by this work, a Pd-catalyzed decarboxylative coupling of oxalate monoester salts with aryl halides was developed by Liu (Scheme 1, method a).[12] However, this procedure requires the presence of a bidentate phosphine ligand (dppp or dCypp). It is worth noting that this reaction, starting from iodobenzene and some activated bromobenzene derivatives, was successfully catalyzed under ligand free conditions.[13] In both protocols, the reaction was performed at 150 °C for 24 h in NMP solvent under nitrogen conditions. In addition to these constraints, prior to use, the potassium α-oxocarboxylate has to be first synthesized from diethyloxalate. Gooßen has developed a catalyst system ($Pd(OAc)_2$/ dppp/DABCO) which promotes the decarboxylation of benzyl oxalates to give arylacetates from benzylic alcohols and dialkyl oxalates.[14]



Scheme 1. Palladium-catalyzed carboxylation reactions.

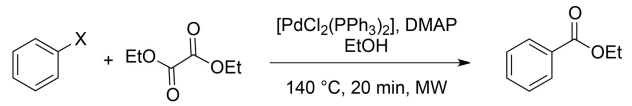
More recently, polystyrene-supported Palladium(0) (Pd@PS) nanoparticles were explored as a heterogeneous catalyst for hydroxycarboxylation of aryl halides

in the presence of oxalic acid under microwave irradiation (Scheme 1, method b).[15]

In this context, we wish to describe herein an efficient microwave-promoted ethoxycarbonylation of aromatic and heteroaromatic bromides or chlorides via Pd-catalyzed with the commercial available diethyloxalate as CO source.

Our first attempt to evaluate the feasibility of the reaction was realized starting from bromobenzene **1a** in the presence of diethyl oxalate **2** (2 equiv.), 1.3 mol% of $PdCl_2(PPh_3)_2$ and dimethylaminopyridine DMAP (1.2 equiv.) and ethanol (1.5 equiv.) (Table 1). The reaction was then irradiated by microwave for 20 min at 140 °C. It is important to note that the pressure increased rapidly due to gas release when the temperature reached 130 °C. The expected ethyl benzoate **3** was obtained in 79% yield (entry 1, Table 1). Hence, encouraged by this first result, investigations were performed to determine the optimal conditions. The amount of ethanol as addictive was first evaluated. The results revealed that the presence of ethanol was crucial for the reaction and increasing its amount to 3 equiv. improved the yield to 97% (46% vs 97% yield, entry 3 vs entry 2, Table 1).

Table 1. Optimization of the reaction conditions starting from halogenobenzene **1a–c**.[a]



Entry	1	X	[Pd] mol%	2 (eq)	Yield (%)[b]
1[c]	**1a**	Br	1.3	6.8	79
2	**1a**	Br	1.3	6.8	97
3[d]	**1a**	Br	1.3	6.8	46
4[e]	**1a**	Br	1.3	6.8	9
5	**1a**	Br	1.3	2.1	89
6	**1a**	Br	1.3	1.2	92
7	**1a**	Br	0.65	1.2	97 (85)[f]
8	**1a**	Br	0.3	1.2	95
9[g]	**1a**	Br	0.65	1.2	0
10[h]	**1a**	Br	0.65	1.2	75
11	**1b**	Cl	0.65	1.2	0
12	**1c**	I	0.65	1.2	85

[a] Reaction conditions: **1** (1 mmol), **2**, $PdCl_2(PPh_3)_2$, DMAP (1.2 mmol), EtOH (3 mmol) at 140 °C for 20 min under microwave irradiation.
[b] GC yield with diphenylmethane as internal standard.
[c] EtOH (1.5 mmol).
[d] Reaction performed without EtOH.
[e] Reaction performed using NMP as solvent (3 mmol).
[f] Isolated yield.
[g] Reaction performed at 120 °C.
[h] Reaction performed for 10 min.

Unlike previous studies,[12,13] the use of NMP as solvent led to a very limited reactivity (entry 4). In addition, it appeared that decreasing the amount of diethyl oxalate or the loading of catalyst was slightly beneficial to the yield (entry 5 *vs* 6 and entry 6 *vs* 7 respectively). It has to be noted that no reaction occurred and the vial pressure did not increased when the reaction was performed at 120 °C (entry 9). This result supported the assumption that a higher temperature was then necessary for the required decomposition of diethyloxalate. Furthermore, a lower yield was obtained when the reaction was carried out for 10 min (entry 10). Replacing the bromine atom by chlorine or iodine atoms led to an absence of reactivity (entry 11) or a slight decrease in yield (entry 12).

The reaction was then carried out with various bases (entries 1 to 5, Table 2) and Pd sources (entries 7 to 10, Table 2). It appeared that the presence of a mesomeric effect in the base is necessary to obtain good yields. Indeed, higher yields were obtained using dimethylaminopyridine (DMAP), 1,8-diazabicycloundec-7-ene (DBU) (entries 1–2).

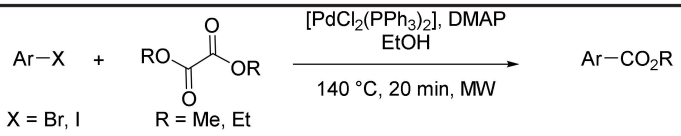
Table 2. Screening of base and catalyst starting from bromobenzene **1a**.[a]

Entry	[Pd]	Base[b]	Yield (%)[c]
1	$PdCl_2(PPh_3)_2$	DMAP	97
2	$PdCl_2(PPh_3)_2$	DBU	53
3	$PdCl_2(PPh_3)_2$	TMG	34
4	$PdCl_2(PPh_3)_2$	DIPEA	0
5	$PdCl_2(PPh_3)_2$	TEA	22
6[d]	$PdCl_2(PPh_3)_2$	DMAP	48
7	$PdCl_2$	DMAP	70
8	Pd/C	DMAP	8
9	$Pd(OAc)_2$	DMAP	95
10	$Pd(TFA)_2$	DMAP	95

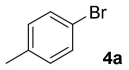
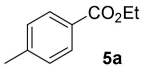
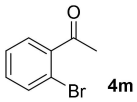
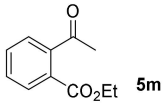
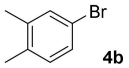
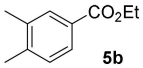
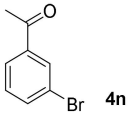
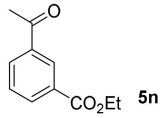
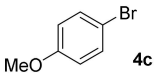
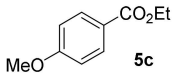
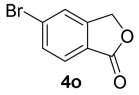
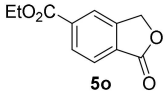
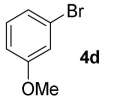
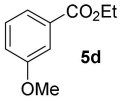
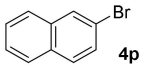
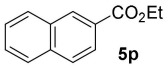
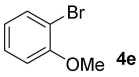
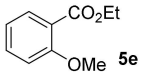
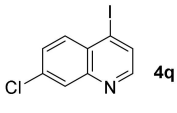
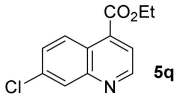
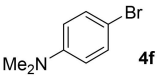
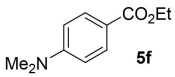
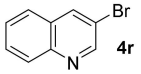
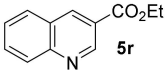
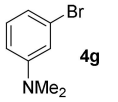
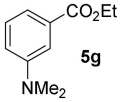
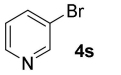
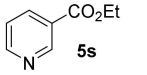
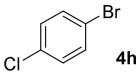
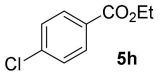
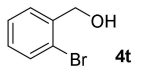
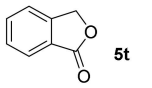
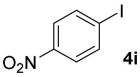
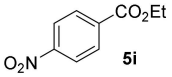
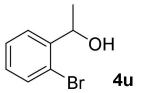
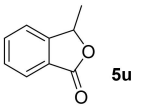
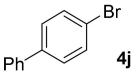
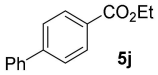
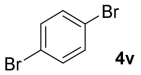
[a] Reaction conditions: **1a** (1 mmol), **2** (1.2 mmol), [Pd] (0.6 mol%), base (1.2 mmol), EtOH (3 mmol) at 140 °C for 20 min under microwave irradiation.
[b] DBU = 1,8-diazabicyclo undec-7-ene, TMG = tetramethylguanidine, DIPEA = di isopropylethylamine, TEA = triethylamine.
[c] GC yields with diphenylmethane as internal standard.
[d] Reaction performed with 0.6 mmol of DMAP.

With the optimal reaction conditions in hand, we next turned our effort to examine the substrate scope of the ethoxycarbonylation with a good number of diversely substituted aryl bromides and some aryl iodides (Table 3). As shown in Table 3, a broad range of aryl bromides carrying electron-donating and electron-attracting substituents reacted smoothly with diethyl oxalate in good to excellent isolated yields. Lower yields observed for starting compounds **4f**, **4h** and **4i** arised from the nucleophilic substitution of

Table 3. Scope of the ethoxycarbonylation of bromo- and iodoarenes under optimal conditions.[a]



4 **2** **5**

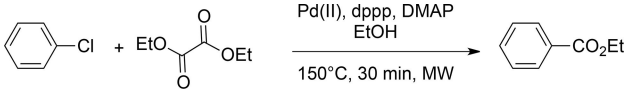
Entry	Substrate **4**	Product **5**	Yield [%][b]	Entry	Substrate **4**	Product **5**	Yield [%][b]
1	 **4a**	 **5a**	87	13	 **4m**	 **5m**	60
2	 **4b**	 **5b**	80	14	 **4n**	 **5n**	87
3	 **4c**	 **5c**	94	15	 **4o**	 **5o**	75
4	 **4d**	 **5d**	95	16	 **4p**	 **5p**	92
5	 **4e**	 **5e**	82	17	 **4q**	 **5q**	55
6	 **4f**	 **5f**	55	18	 **4r**	 **5r**	41
7	 **4g**	 **5g**	93	19	 **4s**	 **5s**	66
8	 **4h**	 **5h**	70	20	 **4t**	 **5t**	77
9	 **4i**	 **5i**	60	21	 **4u**	 **5u**	88
10	 **4j**	 **5j**	97	22	 **4v**	**5k**	63
11	**4k**	**5k**	77	23[c]	**1a**	**5w**	88
12	**4l**	**5l**	87	24[d]	**1a**	**5x**	95

[a] *Reaction conditions*: **4** (1 mmol), **2** (1.2 mmol), $PdCl_2(PPh_3)_2$ (0.6 mol%), DMAP (1.2 mmol), EtOH (3 mmol) at 140 °C for 20 min under microwave irradiation.
[b] Isolated yields.
[c] Reaction performed using dimethyloxalate (1.2 mmol) in MeOH (3 mmol). [d] Reaction performed using H_2O as solvent (3 mmol).

dimethylamino, chloro and nitro substituents by ethanol. Halogenated heterocycles such as quinoline and pyridine gave moderate to good yields of the corresponding esters **5q–s** (entries 17–19). A wide range of functional groups including ester, ketone, amide were tolerated. The esters **5k–o** were obtained in good yields ranging from 60 to 87% (entries 11–15). The chemoselective ethoxycarbonylation was observed for **4h** to produce **5h** (entry 8). A lactonization was occurred in the presence of an alcohol function in the ortho position in **4t** and **4u.** The isobenzofuranone **5t** and **5u** were obtained in excellent yields of 77 and 88% respectively (entries 20 and 21). When the reaction was performed in the presence of dimethyloxalate starting from **1a**, methylbenzoate **5w** was obtained in 88% yield (entry 23). Besides, the use of water as solvent led to the formation of benzoic acid **5x** in excellent yield of 95% (entry 24).

Even though the above conditions could not be applied from chlorobenzene **1b** (Table 1, entry 11), we found that the addition of a ligand such as dppp was beneficial for its alkoxycarbonylation (Table 4). Further optimization of the conditions revealed that the reaction has to be conducted at 150 °C for 30 min, in the presence of 3 mol% of $PdCl_2(PPh_3)_2$ to furnish ester **3a** in 85% yield (Table 4, entry 6). These conditions were then applied to some aryl chlorides leading to the corresponding aryl esters in good yields ranging from 50 to 78% (Table 5).

Table 4. Optimization of the reaction conditions starting from chlorobenzene.[a]

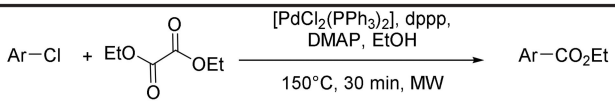


1b **2** **3**

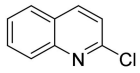
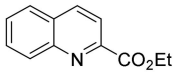
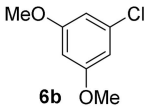
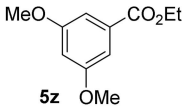
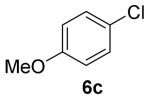
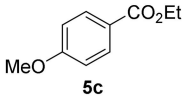
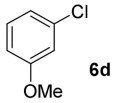
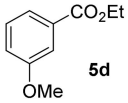
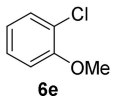
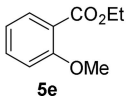
Entry	T (°C)	Time (min)	[Pd] (mol%)	[dppp][b] (mol%)	Yield (%)[c]
1	140	20	$PdCl_2(PPh_3)_2$ (0.7)	–	0
2	140	20	$PdCl_2(PPh_3)_2$ (0.7)	1.5	35
3	150	30	$PdCl_2(PPh_3)_2$ (1.5)	3	61
4	150	30	$PdCl_2$ (1.5)	3	46
5	150	30	$Pd(OAc)_2$ (1.5)	3	15
6	150	30	$PdCl_2(PPh_3)_2$ (3)	6	85

[a] Reaction conditions: **1b** (1 mmol), **2** (1.2 mmol), DMAP (1.2 mmol), Pd catalyst, dppp, EtOH (3 mmol) under microwave irradiation.
[b] dppp = 1,3-bis-(diphenylphosphine)propane.
[c] GC yield with diphenylmethane as internal standard.

Table 5. Scope of the ethoxycarbonylation of chloroarenes under optimal conditions.[a]



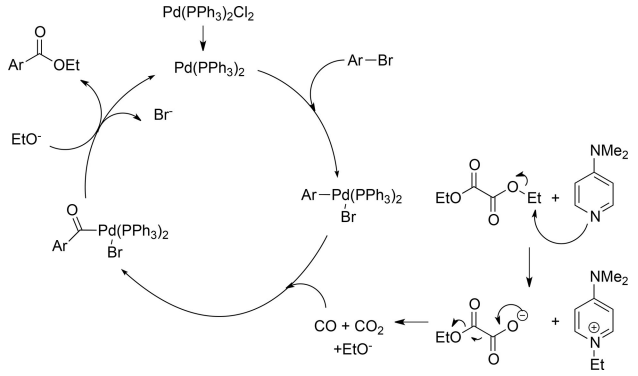
6 **2** **5**

Entry	Substrate	Product	Yield (%)[b]
1	 **6a**	 **5y**	71
2	 **6b**	 **5z**	78
3	 **6c**	 **5c**	65
4	 **6d**	 **5d**	71
5	 **6e**	 **5e**	50

[a] Reaction conditions: **6** (1 mmol), **2** (1.2 mmol), DMAP (1.2 mmol), $PdCl_2(PPh_3)_2$ (0.03 mmol), dppp (0.06 mmol), EtOH (3 mmol) at 150 °C for 30 min under microwave irradiation.
[b] Isolated yields.

Although a detailed mechanistic picture requires further studies, results described above allow us to suggest a plausible reaction pathway presented in Scheme 2. In a first step, monosubstituted oxalate was obtained by reaction of conjugated bases such as DMAP or DBU with diethyloxalate.[16] From theorical calculations, Fu and Liu have proposed a mechanism based on the coordination of oxalate with Pd(II) which was then subjected to a decarboxylation to give the ester.[12] In our experimental conditions, we can suggest that the decomposition of oxalate to produce CO and CO_2 in closed vessel is mechanistically similar to that reported earlier by Das and co-workers.[15] Gas chromatographic analysis of the reaction medium displayed characteristic peaks of CO and CO_2 (see supporting information). Indeed, ester **3** was obtained

in only 7% when the reaction was performed with monosubstituted oxalate. CO is then inserted into the Pd(II)-Ar bond via a coordination with the metal. Ligand exchange of bromide by ethanolate or ethanol and reductive elimination give the ester. It is worth noting that, when the reaction was performed in the presence of diethyloxalate and methanol as solvent, a mixture of methyl- and ethylesters was obtained in a 1/3 ratio. This result confirms that both ethanol and ethanolate could react in the ligand exchange step or in a transesterification reaction.



Scheme 2. Proposed mechanism.

In conclusion, we developed a new Palladium(II)-catalyzed ethoxycarbonylation of aryl bromides with alkyl oxalate as carbon monoxide source. This method presents many advantages: microwave activation, non-toxic solvent, no additional ligand, extended to aryl chlorides, no nitrogen atmosphere. In consequence, this method illustrates an inexpensive and operationally simple method for the preparation of aromatic esters.

Experimental Section

General Procedure

Bromobenzene **1a** (157 mg, 1 mmol), diethyloxalate **2** (180 mg, 1.2 mmol), DMAP (153 mg, 1.2 mmol), $PdCl_2(PPh_3)_2$ (4.7 mg, 6.10^{-3} mmol) were taken in an oven-dried test tube equipped with a magnetic stir bar and a **Teflon** screw-**cap** using EtOH (142 mg, 3 mmol) as solvent. The reaction mixture was then irradiated in a closed vessel monomode microwave at 140 °C for 20 min. At 130 °C, the pressure reached 5–7 bar. After cooling to ambient temperature, an aqueous solution HCl 1 M (5 mL) was added and the reaction mixture was extracted with diethyl ether (3 × 10 mL). The combined organic layers were dried over $MgSO_4$ and evaporated under reduced pressure. The purification by chromatography over silica gel afforded methyl benzoate ester **3a** as oil (128 mg, 85%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05 (dd, J = 8.4 and 1.5 Hz, 2H), 7.54 (m, 1H), 7.42 (m, 2H), 4.37 (t, J = 7.2 Hz, 2H), 1.39 (t, J = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.6, 132.7, 130.5, 129.5,128.3, 60.9, 14.3.

Acknowledgements

Chevreul institute (*FR 2638*), *Ministère de l'Enseignement Supérieur et de la Recherche*, *Région Nord – Pas de Calais and FEDER are acknowledged for supporting and funding this work.*

References

[1] For reviews see: a) H. Neumann, M. Beller, *Angew. Chem., Int. Ed.* **2009**, *48*, 4114–4133; b) C. F. J. Barnard, *Organometallics* **2008**, *27*, 5402–5422; c) A. Brennfuhrer, X. F. Wu, H. Neumann, M. Beller, *Chem. Soc. Rev.* **2011**, *40*, 4986–5009. d) X. F. Wu, H. Neumann, M. Beller, *Chem. Rev.* **2013**, *113*, 1–35; e) B. Gabriele, R. Mancuso, G. Salerno, *Eur. J. Org. Chem.* **2012**, 6825–6839; f) Q. Liu, H. Zhang, A. Lei, *Angew. Chem. Int. Ed.* **2011**, *50*, 10788–10799.

[2] T. Morimoto, K. Kakiuchi, *Angew. Chem. Int. Ed.* **2004**, *43*, 5580–5588.

[3] a) L. R. Odell, F. Russo, M. Larhed, *Synlett* **2012**, 685–698; b) Y. Wan, M. Alterman, M. Larhed, A. Hallberg, *J. Org. Chem.* **2002**, *67*, 6232–6235; c) J. Wannberg, M. Larhed, *J. Org. Chem.* **2003**, *68*, 5750–5753; d) Z. Wang, Y. Li, F. Zhu, X. F. F. Wu, *Adv. Synth. Catal.* **2016**, *358*, 2855–2859.

[4] a) G. Makado, T. Morimoto, Y. Sugimoto, K. Tsutsumi, N. Kagawa, K. Kakiuchi, *Adv. Synth. Catal.* **2010**, *352*, 299–304; b) A. Kopfer, B. Sam, B. Breit, M. J. Krische, *Chem. Sci.* **2013**, *4*, 1876–1880; c) Q. Liu, K. Yuan, P.-B. Arockiam, R. Franke, H. Doucet, R. Jackstell, M. Beller, *Angew. Chem., Int. Ed.* **2015**, *54*, 4493–4497; d) K. Natte, A. Dumrath, H. Neumann, M. Beller, *Angew. Chem. Int. Ed.* **2014**, *53*, 10090–10094; e) T. Morimoto, K. Fuji, K. Tsutsumi, K. Kakiuchi, *J. Am. Chem. Soc.* **2002**, *124*, 3806–3807; f) T. Shibata, N. Toshida, K. Takagi, *Org. Lett.* **2002**, *4*, 1619–1621; g) W. Li, X. F. Wu, *J. Org. Chem.* **2014**, *79*, 10410–10416;

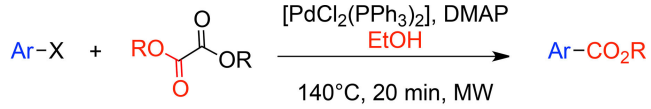
[5] D. S. Friis, R. H. Taaning, A. T. Lindhardt, T. Skrydstrup, *J. Am. Chem. Soc.* **2011**, *133*, 18114–18117.

[6] a) N. Lugan, G. Lavigne, J.-M. Soulie, S. Fabre, P. Kalck, J.-Y. Saillard, J. Francois Halet, *Organometallics* **1995**, *14*, 1712–1731; b) H. W. Lee, A. S. C. Chana, F. Y. Kwong, *Chem. Commun.* **2007**, 2633–2635; c) T. Cochet, V. Bellosta, A. Greiner, D. Roche, J. Cossy, *Synlett* **2011**, 1920–1922; d) T. Ueda, H. Konishi, K. Manabe, *Org. Lett.* **2013**, *15*, 5370–5373; e) P. H. Gehrtz, V. Hirschbeck, I. Fleischer, *Chem. Commun.* **2015**, *51*, 12574–12577; f) H. Konishi, T. Ueda, T. Muto, K. Manabe, *Org. Lett.* **2012**, *14*, 4722–4725; g) I. Fleischer, R. Jennerjahn, D. Cozzula, R. Jackstell, R. Franke, M. Beller, *ChemSusChem* **2013**, *6*, 417–420; h) H. Koniski, H. Nagase, K. Manabe, *Chem. Commun.* **2015**, *51*, 1854–1857; i) H. Li, H. Neumann, M. Beller, X. F. Wu *Angew Chem. Int. Ed.* **2014**, *53*,3183–3186; j) Y. Kata-

fuchi, T. Fujihara, T. Iwai, J. Terao, Y. Tsuji, *Adv. Synth. Catal.* **2011**, *353*, 475–482.
[7] a) M. G. Mura, L. D. Luca, G. Giacomelli, A. Porcheddu, *Adv. Synth. Catal.* **2012**, *354*, 3180–3186; b) X. Qi, C. L. Li, X. F. Wu *Chem. Eur. J.* **2016**, *22*, 5835–5838.
[8] a) E. A. Jo, J. H. Lee, C. H. Jun, *Chem. Commun.* **2008**, 5779–5781; b) S. H. Christensen, E. P. K. Olsen, J. Rosenbaum, R. Madsen, *Org. Biomol. Chem.* **2015**, *13*, 938–945; c) J. J. Verendel, M. Nordlund, P. G. Andersson, *ChemSusChem* **2013**, *6*, 426–429.
[9] B. H. Min, D. S. Kim, H. S. Park, C. H. Jun, *Chem. Eur. J.* **2016**, *22*, 6234–6238.
[10] a) L. J. Gooßen, F. Rudolphi, C. Oppel, N. Rodriguez, *Angew. Chem. Int. Ed.* **2008**, *47*, 3043–3045. b) L. J. Gooßen, B. Zimmermann, C. Linder, N. Rodriguez, P. P. Lange, J. Hartung, *Adv. Synth. Catal.* **2009**, *351*, 2667–2674.
[11] a) P. Fang, M. Li, H. Ge, *J. Am. Chem. Soc.* **2010**, *132*, 11898–11899. b) C. Pan, H. Jin, X. Liu, Y. Cheng, C. Zhu, *Chem. Commun.* **2013**, *49*, 2933–2935.
[12] R. Shang, Y. Fu, J. B. Li, S. L. Zhang, Q. X. Guo, L. Liu, *J. Am. Chem. Soc.* **2009**, *131*, 5738–5739.
[13] Y. Li, H. H. Chen, C. F. Wang, X. L. Xu, Y. S. Feng, *Tetrahedron Lett.* **2012**, *53*, 5796–5799.
[14] M. F. Grünberg, L. J. Gooßen, *Chem. Eur. J.* **2013**, *19*, 7334–7337.
[15] A. K. Shil, S. Kumar, C. B. Reddy, S. Dadhwal, V. Thakur, P. Das, *Org. Lett.* **2015**, *17*, 5352–5355.
[16] K. Massonne, J. Sundermeyer, A. Braam, U.S. Pat. Appl. Publ., US 20140099249A1 20140410, 2014.

UPDATES

Diethyloxalate as "CO" Source for Palladium-Catalyzed Ethoxycarbonylation of Bromo- and Chloroarene Derivatives



X = Br, I R = Me, Et

Adv. Synth. Catal. **2017**, *359*, 1–7

A. Monrose, H. Salembier, T. Bousquet, S. Pellegrini*, L. Pélinski*