C. R. Chimie 17 (2014) 1184–1189

Contents lists available at ScienceDirect

Comptes Rendus Chimie

www.sciencedirect.com

Full paper/Mémoire

Influence of the solvent and of the reaction concentration for palladium-catalysed direct arylation of heteroaromatics with 4-bromoacetophenone

Influence du solvant et de la concentration pour l'arylation directe catalysée au palladium d'hétéroaromatiques par la 4-bromoacétophénone

Souhila Bensaid, Henri Doucet *

Institut des sciences chimiques de Rennes, UMR 6226 CNRS–Université de Rennes-1, « Catalyse et Organometalliques », campus de Beaulieu, 35042 Rennes cedex, France

ARTICLE INFO

Article history:
Received 23 January 2014
Accepted after revision 17 February 2014
Available online 7 October 2014

Keywords:
Aryl bromides
Catalysis
C–H activation
Heteroaromatics
Palladium
Concentration

Mots clés :
Bromures d'aryle
Catalyse
Activation C–H
Hétéroaromatiques
Palladium
Concentration

ABSTRACT

The solvent is certainly one of the main sources of wastes during palladium-catalysed direct arylation reactions. We found that such direct arylations of heteroaromatics can be performed using very high concentrations of reactants (0.5 M–5 M). However, the Pd catalyst precursor used must be adapted to both the solvent nature and the concentration of reactants. The reactions performed in DMA, NMP or DMF can be carried out in very concentrated reaction mixtures using 0.1 mol% $Pd(OAc)_2$ catalyst without phosphine ligand. On the other hand, the reactions in CPME, pentan-1-ol or diethylcarbonate should be performed with a palladium catalyst associated with a phosphine ligand. These reaction conditions allow us to reduce the amount of wastes formed in the course of these couplings.

RÉSUMÉ

Le solvant est certainement l'une des principales sources de déchets lors des réactions d'arylation directes d'hétéroaromatiques catalysées au palladium. Nous avons constaté que ces réactions peuvent être réalisées en utilisant des concentrations très élevées (0,5 M–5 M). Cependant, le catalyseur de palladium utilisé doit être adapté à la fois à la nature du solvant et à la concentration des réactifs. Les réactions effectuées dans le DMA, la NMP ou le DMF peuvent être réalisées dans des mélanges réactionnels très concentrés, en utilisant 0,1 mol % de $Pd(OAc)_2$ sans addition de ligand de type phosphine. En revanche, les réactions dans le CPME, le pentan-1-ol ou le carbonate de diéthyle doivent être effectuée avec un catalyseur de palladium associé à un ligand phosphine. Ces conditions réactionnelles permettent de réduire la quantité de déchets formés au cours de ces couplages.

* Corresponding author.
E-mail address: henri.doucet@univ-rennes1.fr (H. Doucet).

1631-0748/$ – see front matter
http://dx.doi.org/10.1016/j.crci.2014.02.004

1. Introduction

The synthesis of arylated heteroaromatics is an important field for research in organic synthesis due to the physical or biological properties of these compounds. In 1990, Ohta et al. reported that the direct arylation of several heteroaromatics with aryl halides proceed in moderate to good yields using $Pd(PPh_3)_4$ as the catalyst and DMA (*N*,*N*-dimethylacetamide) as the solvent [1]. Since these very innovative results, the Pd-catalysed direct arylation of heteroaromatics with aryl halides or pseudo-halides has been demonstrated to be an extremely powerful method for the synthesis of a variety of arylated heterocycles in a few steps [2]. This reaction provides a cost-effective access to such compounds. Moreover, the major wastes of the reaction are a base associated with HX and the reaction solvent, instead of metallic salts produced under classical cross-coupling procedures, such as Suzuki, Negishi or Stille reactions [3]. The method avoids the preliminary preparation of an organometallic compound, reducing the number of steps necessary to prepare these compounds. However, these coupling reactions are generally performed using large amounts of relatively toxic solvents, such as DMA, DMF, NMP, or dioxane [4–6]. In recent years, a few solvents that can be considered as "greener"[7] according to P. Anastas' principles have been employed for direct arylations [8]. For example, Greaney and Djakovitch reported that, using water as a solvent, the direct arylation of oxazoles, thiazoles, indazoles, or indoles proceeds nicely [9]. René and Fagnou employed a mixture of water and EtOAc for the direct arylation of thiophenes [10a]. Polyethylene glycol (PEG 20000) has been found to promote the direct arylation of triazoles [10b]. Carbonates, ethers or alcohols have also been successfully employed for the direct arylation of some heteroaromatics [11]. The ruthenium-catalysed direct arylation of 2-arylpyridines in carbonates or water has been reported by Fischmeister, Dixneuf et al. [12].

Waste prevention is a major requirement in current organic synthesis. One of the most promising approaches to reduce the formation of wastes is solvent-free reactions or highly concentrated reaction media [13,14]. Such conditions make syntheses easier due to the reduction in reactor size and to simpler work-up, as there is less solvent to eliminate at the end of the reaction. Therefore, the use of such conditions for Pd-catalysed direct arylations would be environmentally attractive for the preparation of arylated heteroarenes.

To our knowledge, the influence of the reaction concentration using various solvents for the palladium-catalysed direct arylation of heteroaromatics has not yet been studied. Herein, we wish to report on the palladium-catalysed direct arylations of a range of heteroaromatic derivatives with an aryl bromide, using a set of solvents under various reaction concentrations.

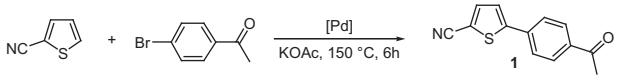
2. Results and discussion

For this study, six solvents were employed. DMA and DMF, which are classified as "undesirable" solvents for industrial application, NMP, which is "usable", and also pentan-1-ol, cyclopentylmethylether (CPME) and diethylcarbonate, which are among the "preferred" solvents [15].

The use of CPME as a solvent presents several advantageous features, such as a high hydrophobicity. Its limited miscibility in water allows an easy separation and recovery from water. Another preferable characteristic is the low formation of peroxides compared to THF or diisopropyl ether. Moreover, CPME can be manufactured by the addition of MeOH to cyclopentene, which produces no apparent waste [16]. Pentan-1-ol is not considered a hazardous air-pollutant solvent, is readily biodegradable and practically non-toxic to fish and aquatic organisms. Pentan-1-ol can be prepared by the reduction of 1-valeraldehyde with hydrogen or by fermentation and is present in cider, beer or wine to varying degrees. Therefore, exposure to residual amounts of this alcohol is unlikely to have any adverse health effects. Diethylcarbonate is a polar, aprotic, non-toxic, and biodegradable solvent [17]. Based on these properties, it also offers an environmentally friendly alternative to standard polar solvents. Therefore, the use of CPME, pentan-1-ol or diethylcarbonate as solvents is in agreement with the principles 1, 5 and 12 of "green chemistry" [7].

We have recently reported that the phosphine-free $Pd(OAc)_2$ catalyst promotes very efficiently the direct arylation of some heteroaromatics in DMA [18]. We initially employed this phosphine-free procedure in order to determine the influence of the amount and nature of the solvent for Pd-catalysed direct arylations. A first set of reactions using thiophene 2-carbonitrile (0.75 mmol) and 4-bromoacetophenone (0.5 mmol) as the coupling partners was carried out under previously reported reaction conditions [18], but in 4, 1 or 0.5 mL of solvent with only 0.1 mol% $Pd(OAc)_2$ catalyst (Table 1, column 3). In the presence of polar solvents, DMA, NMP and DMF, high conversions of 4-bromoacetophenone and yields of coupling product **1** were obtained (Table 1, entries 1–3, 5–7 and 9–11 in column 3). The use of 0.1 mL of these three solvents (concentration 5 M) and again 0.1 mol% $Pd(OAc)_2$ catalyst led to lower conversion rates of 4-bromoacetophenone of 36, 30 and 66% (Table 1, entries 4, 8 and 12 in column 3). Then, we employed 0.1–4 mL of pentan-1-ol, diethylcarbonate or CPME as the solvent and again 0.1 mol% $Pd(OAc)_2$ catalyst. In all cases, poor conversions of 4-bromoacetophenone were obtained (Table 1, entries 13–24 in column 3). The use of a higher catalyst loading of 0.5 mol% $Pd(OAc)_2$ catalyst was found to increase the conversion of 4-bromoacetophenone for the reactions performed in 0.1 mL of DMA or NMP (Table 1, entries 4 and 8 in column 4), whereas it was not profitable for reactions performed in pentan-1-ol and less profitable for reactions performed in diethylcarbonate (Table 1, entries 14–16, 19, and 20 in column 4). With this ligand-free catalyst, under higher palladium concentrations, the so-called "palladium black" forms more rapidly when pentan-1-ol or diethylcarbonate are used as the solvents. Therefore, the concentration of active palladium species is not increased, and the conversions of 4-bromoacetophenone are not improved. This ligand-free procedure has to be employed only with solvents that display coordination properties with palladium. Therefore, in order to obtain higher yields

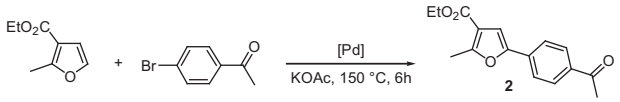
Table 1
Influence of the solvent nature and of the concentration on the Pd-catalysed 5-arylation of thiophene 2-carbonitrile with 4-bromoacetophenone.



Entry	Solvent (mL)	$Pd(OAc)_2$ (0.1 mol%) Conv. (%)	$Pd(OAc)_2$ (0.5 mol%) Conv. (%)	$PdCl(C_3H_5)(dppb)$ (0.1 mol%) Conv. (%)	$PdCl(C_3H_5)(dppb)$ (0.5 mol%) Conv. (%)
1	DMA (4)	100 (88)			
2	DMA (1)	100			
3	DMA (0.5)	100 (85)			
4	DMA (0.1)	36	74	54	100 (82)
5	NMP (4)	73			
6	NMP (1)	100			
7	NMP (0.5)	100 (83)			
8	NMP (0.1)	30	63		
9	DMF (4)	100			
10	DMF (1)	100			
11	DMF (0.5)	100 (80)			
12	DMF (0.1)	66	42	25	
13	Pentan-1-ol (4)	0			
14	Pentan-1-ol (1)	19	3		
15	Pentan-1-ol (0.5)	19	8	48	100 (76)
16	Pentan-1-ol (0.1)	12	9	39	97
17	Diethylcarbonate (4)[a]	0			
18	Diethylcarbonate (1)[a]	0			62
19	Diethylcarbonate (0.5)[a]	3	4		68 (56)
20	Diethylcarbonate (0.1)[a]	15	24		60
21	Cyclopentyl methyl ether (4)[b]	0			
22	Cyclopentyl methyl ether (1)[b]	0		15	100 (81)
23	Cyclopentyl methyl ether (0.5)[b]	5			84
24	Cyclopentyl methyl ether (0.1)[b]	10			67

Conditions: 4-bromoacetophenone (0.5 mmol), thiophene 2-carbonitrile (0.75 mmol), KOAc (1 mmol), 6 h, 150 °C, isolated yield in parentheses.
[a] Reaction temperature: 130 °C.
[b] Reaction temperature: 125 °C.

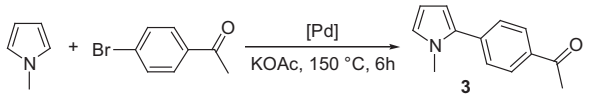
Table 2
Influence of the solvent nature and of the concentration on the Pd-catalysed 5-arylation of ethyl 2-methylfuran-3-carboxylate with 4-bromoacetophenone.



Entry	Solvent (mL)	$Pd(OAc)_2$ (0.1 mol%) Conv. (%)	$Pd(OAc)_2$ (0.5 mol%) Conv. (%)	$PdCl(C_3H_5)(dppb)$ (0.1 mol%) Conv. (%)	$PdCl(C_3H_5)(dppb)$ (0.5 mol%) Conv. (%)
1	DMA (1)	100			
2	DMA (0.5)	100 (87)			
3	DMA (0.1)	14	100	42	100 (82)
4	NMP (1)	79	100		
5	NMP (0.5)	58	100 (85)		
6	NMP (0.1)	11	100		
7	DMF (1)	100			
8	DMF (0.5)	57	100 (82)		
9	DMF (0.1)	4	47		100 (80)
10	Pentan-1-ol (1)	41			
11	Pentan-1-ol (0.5)	34			100 (81)
12	Pentan-1-ol (0.1)	3	40	26	
13	Diethylcarbonate (1)[a]	0	0	2	6
14	Diethylcarbonate (0.5)[a]	0	2	2	32
15	Diethylcarbonate (0.1)[a]	10	2	7	100 (76)
16	Cyclopentyl methyl ether (1)[b]	0	0	1	4
17	Cyclopentyl methyl ether (0.5)[b]	0	0	2	23
18	Cyclopentyl methyl ether (0.1)[b]	5	0	5	100 (84)

Conditions: 4-bromoacetophenone (0.5 mmol), ethyl 2-methylfuran-3-carboxylate (0.75 mmol), KOAc (1 mmol), 6 h, 150 °C, isolated yield in parentheses.
[a] Reaction temperature: 130 °C.
[b] Reaction temperature: 125 °C.

Table 3
Influence of the solvent nature and of the concentration on the Pd-catalysed 2-arylation of 1-methylpyrrole with 4-bromoacetophenone.



Entry	Solvent (mL)	$Pd(OAc)_2$ (0.1 mol%) Conv. (%)	$Pd(OAc)_2$ (0.5 mol%) Conv. (%)	$PdCl(C_3H_5)(dppb)$ (0.5 mol%) Conv. (%)
1	DMA (1)	100		
2	DMA (0.5)	100 (78)		
3	DMA (0.1)	97		
4	NMP (1)	100		
5	NMP (0.5)	100 (75)		
6	NMP (0.1)	100		
7	DMF (1)	100		
8	DMF (0.5)	100 (76)		
9	DMF (0.1)	48	89	
10	Pentan-1-ol (1)	24	34	
11	Pentan-1-ol (0.5)	15	21	
12	Pentan-1-ol (0.1)	4	4	88 (61)
13	Diethylcarbonate (1)[a]	4	3	
14	Diethylcarbonate (0.5)[a]	3	3	28
15	Diethylcarbonate (0.1)[a]	6	5	100 (66)
16	Cyclopentyl methyl ether (1)[b]	2	0	
17	Cyclopentyl methyl ether (0.5)[b]	1	3	
18	Cyclopentyl methyl ether (0.1)[b]	3	4	

Conditions: 4-bromoacetophenone (0.5 mmol), 1-methylpyrrole (1.5 mmol), KOAc (1 mmol), 6 h, 150 °C, isolated yield in parentheses.
[a] Reaction temperature: 130 °C.
[b] Reaction temperature: 125 °C.

with pentan-1-ol, diethylcarbonate or CPME solvents, we employed 0.1 or 0.5 mol% $PdCl(C_3H_5)(dppb)$ as the catalyst. In pentan-1-ol, much better results were obtained, even in the presence of only 0.1 mL of solvent (concentration 5 M) (Table 1, entries 14–16 in columns 5 and 6). For reactions in diethylcarbonate, similar conversions of 60–68% of 4-bromoacetophenone were obtained using 1, 0.5 or 0.1 mL of solvent and 0.5 mol% $PdCl(C_3H_5)(dppb)$ (Table 1, entries 18–20 in column 6). For the reactions in CPME, the best results were obtained using 1 or 0.5 mL of solvent (Table 1, entries 22–24 in column 6). In summary, the phosphine-free procedure can be employed with DMA, NMP and DMF as the solvents, whereas the use of $PdCl(C_3H_5)(dppb)$ catalyst [dppb: 1,4-bis(diphenylphosphino)butane] appears to be more reliable for reactions in pentan-1-ol, diethylcarbonate or CPME. For most of these solvents, reaction concentrations of 1 M can be employed.

Then, we studied the 5-arylation of a furan derivative with these six solvents at different concentrations (Table 2). In general, furan derivatives are less reactive than thiophenes for Pd-catalysed direct arylations [11e]. With 1 mL of DMA, NMP or DMF, 0.5 mmol of 4-bromoacetophenone (concentration 0.5 M) and 0.1 mol% $Pd(OAc)_2$ catalyst, high or complete conversions of 4-bromoacetophenone were observed (Table 2, entries 1, 4 and 7, column 3). On the other hand, the use of only 0.1 mL of solvent for 0.5 mmol of aryl bromide (concentration 5 M) led to poor conversions in these three solvents (Table 2, entries 3, 6 and 9, column 3). Again, the reactions performed in pentan-1-ol, diethylcarbonate or CPME using $Pd(OAc)_2$ catalyst led to low conversions of 4-bromoacetophenone (Table 2, entries 10–18, columns 3 and 4), whereas the use of 0.5 mol% $PdCl(C_3H_5)(dppb)$ catalyst and 0.1 or 0.5 mL in these solvents led to good yields of **2** (Table 2, entries 11, 15 and 18, column 6). It should be noted that, for this reaction, with diethylcarbonate or CPME as the solvent, better results were obtained in more concentrated reaction mixtures (5 M or 1 M > 0.5 M).

Finally, the 2-arylation of 1-methylpyrrole with 4-bromoacetophenone was studied using again various amounts of the six solvents (Table 3). The use of 0.1, 0.5 or 1 mL of DMA, NMP or DMF for reaction of 0.5 mmol of 4-bromoacetophenone in the presence of 0.1 mol% $Pd(OAc)_2$ catalyst led to very high or complete conversions of the starting material, in most cases (Table 3, entries 1–8). A moderate conversion of 4-bromoacetophenone was observed in 0.1 mL of DMF, and 0.5 mol% $Pd(OAc)_2$ catalyst had to been employed to obtain a high conversion of the aryl bromide (Table 3, entry 9). As expected, the use of 0.1 or 0.5 mol% of phosphine-free $Pd(OAc)_2$ catalyst in CPME, pentan-1-ol or diethylcarbonate was ineffective, whereas high or complete conversions were obtained in 0.1 mL of pentan-1-ol or diethylcarbonate in the presence of 0.5 mol% $PdCl(C_3H_5)(dppb)$ catalyst (Table 3, entries 10–18).

3. Conclusion

In summary, these results demonstrate that the direct arylation of heteroaromatics can be performed with highly concentrated reaction mixtures (up to 5 M). However, the nature and loading of the catalyst has to be tuned according to the solvent. For reactions in DMA, NMP or DMF, a low loading (0.1–0.5 mol%) of a phosphine-free catalyst promotes the coupling in high yields. On the other

hand, the palladium catalyst associated with a phosphine ligand should be preferred for the reactions performed in CPME, pentan-1-ol or diethylcarbonate. These results demonstrate that most of these couplings proceed nicely using highly concentrated reaction mixtures, even in some solvents that are considered as "green". Such reactions conditions allow industrially viable processes, as they reduce the hazards and toxicity associated with the use of solvents, reduce wastes costs, and simplify the separation procedure at the end of the reaction.

4. Experimental

$Pd(OAc)_2$, $[Pd(C_3H_5)Cl]_2$, dppb, heteroarenes, 4-bromoacetophenone, KOAc (99%) were purchased from Alfa Aesar and were not purified before use. DMA (99 + %), NMP (99 + %), DMF (99 + %), pentan-1-ol (99%), cyclopentyl methyl ether (99 + %) and diethylcarbonate (99%) were purchased from Acros Organics and were not purified before use.

4.1. Preparation of the $PdCl(C_3H_5)$(dppb) catalyst [19]

An oven-dried 40-mL Schlenk tube equipped with a magnetic stirring bar under argon atmosphere was charged with $[Pd(C_3H_5)Cl]_2$ (182 mg, 0.5 mmol) and dppb (426 mg, 1 mmol). Ten millilitres of anhydrous dichloromethane were added, then the solution was stirred at room temperature for 20 min. The solvent was removed under vacuum. The yellow powder was used without purification. ^{31}P NMR (81 MHz, $CDCl_3$) $\delta = 19.3$ (s).

4.2. Representative procedure for coupling reactions

The reaction of 4-bromoacetophenone (0.100 g, 0.5 mmol), heteroaromatic (0.75 mmol) and KOAc (0.098 g, 1 mmol) at 125–150 °C (see tables) in the presence of $PdCl(C_3H_5)$(dppb) or $Pd(OAc)_2$ (see tables) in the appropriate solvent under argon affords the coupling product after filtration on silica gel (pentane/ether).

4.2.1. 5-(4-Acetylphenyl)thiophene-2-carbonitrile (1) [20a]

According to the representative procedure, 4-bromoacetophenone (0.100 g, 0.5 mmol) and thiophene 2-carbonitrile (0.082 g, 0.75 mmol) in 1 mL of cyclopentyl methyl ether afford **1** in 81% yield.

4.2.2. 5-(4-Acetylphenyl)-2-methylfuran-3-carboxylic acid ethyl ester (2) [20b]

According to the representative procedure, 4-bromoacetophenone (0.100 g, 0.5 mmol) and ethyl 2-methylfuran-3-carboxylate (0.116 g, 0.75 mmol) in 0.1 mL of diethylcarbonate afford **2** in 76% yield.

4.2.3. 1-[4-(1-Methyl-1H-pyrrol-2-yl)-phenyl]-ethanone (3) [20c]

According to the representative procedure, 4-bromoacetophenone (0.100 g, 0.5 mmol) and 1-methylpyrrole (0.122 g, 1.5 mmol) in 0.1 mL of diethylcarbonate afford **3** in 66% yield.

Acknowledgements

We thank the CNRS and "Rennes Metropole" for providing financial support.

References

[1] A. Ohta, Y. Akita, T. Ohkuwa, M. Chiba, R. Fukunaga, A. Miyafuji, T. Nakata, N. Tani, Y. Aoyagi, Heterocycles 31 (1990) 1951.
[2] (a) D. Alberico, M.E. Scott, M. Lautens, Chem. Rev. 107 (2007) 174;
(b) T. Satoh, M. Miura, Chem. Lett. 36 (2007) 200;
(c) L.-C. Campeau, D.R. Stuart, K. Fagnou, Aldrichim. Acta 40 (2007) 35;
(d) I.V. Seregin, V. Gevoryan, Chem. Soc. Rev. 36 (2007) 1173;
(e) B.-J. Li, S.-D. Yang, Z.-J. Shi, Synlett (2008) 949;
(f) F. Bellina, R. Rossi, Tetrahedron 65 (2009) 10269;
(g) L. Ackermann, R. Vincente, A.R. Kapdi, Angew. Chem. Int. Ed. 48 (2009) 9792;
(h) X. Chen, K.M. Engle, D.-H. Wang, J.-Q. Yu, Angew. Chem. Int. Ed. 48 (2009) 5094;
(i) J. Roger, A.L. Gottumukkala, H. Doucet, ChemCatChem 2 (2010) 20;
(j) D. Lapointe, K. Fagnou, Chem. Lett. 39 (2010) 1119;
(k) L. Ackermann, Chem. Rev. 111 (2011) 1315;
(l) N. Kuhl, M.N. Hopkinson, J. Wencel-Delord, F. Glorius, Angew. Chem. Int. Ed. 51 (2012) 10236;
(m) J. Wencel-Delord, F. Glorius, Nature Chem. 5 (2013) 369;
(n) K. Yuan, H. Doucet, ChemCatChem 5 (2013) 3495;
(o) B. Li, P.-H. Dixneuf, Chem. Soc. Rev. 42 (2013) 5744;
(p) R. Rossi, F. Bellina, M. Lessi, C. Manzini, Adv. Synth. Catal. 356 (2014) 17.
[3] (a) J.J. Li, G.W. Gribble, Palladium in Heterocyclic Chemistry, Pergamon Press, Amsterdam, 2000;
(b) E. Negishi (Ed.), Handbook of Organopalladium Chemistry for Organic Synthesis, Part III, Wiley-Interscience, New York, 2002, p. 213.
[4] (a) E. David, S. Pellet-Rostaing, M. Lemaire, Tetrahedron 63 (2007) 8999;
(b) H.A. Chiong, O. Daugulis, Org. Lett. 9 (2007) 1449;
(c) P. Amaladass, J.A. Clement, A.K. Mohanakrishnan, Tetrahedron 63 (2007) 10363;
(d) M. Nakano, H. Tsurugi, T. Satoh, M. Miura, Org. Lett. 10 (2008) 1851;
(e) B. Liégault, I. Petrov, S.I. Gorlesky, K. Fagnou, J. Org. Chem. 75 (2010) 1047;
(f) L. Chen, J. Roger, C. Bruneau, P.-H. Dixneuf, H. Doucet, Chem. Commun. 47 (2011) 1872;
(g) K. Yuan, H. Doucet, Chem. Sci. 5 (2014) 392.
[5] (a) M. Parisien, D. Valette, K. Fagnou, J. Org. Chem. 70 (2005) 7578;
(b) E.M. Beccalli, G. Broggini, M. Martinelli, S. Sottocornola, Synthesis (2008) 136;
(c) B. Liégaut, D. Lapointe, L. Caron, A. Vlassova, K. Fagnou, J. Org. Chem. 74 (2009) 1826;
(d) M. Ionita, J. Roger, H. Doucet, ChemSusChem 3 (2010) 367.
[6] (a) F. Bellina, S. Cauteruccio, R. Rossi, Eur. J. Org. Chem. (2006) 1379;
(b) X. Wang, D.V. Gribkov, D. Sames, J. Org. Chem. 72 (2007) 1476;
(c) N. Lebrasseur, I. Larrosa, J. Am. Chem. Soc. 130 (2008) 2926;
(d) P. Ehlers, A. Petrosyan, J. Baumgard, S. Jopp, N. Steinfeld, T.V. Ghochikyan, A.S. Saghyan, C. Fischer, P. Langer, ChemCatChem 5 (2013) 2504;
(e) Y. Xu, L. Zhao, Y. Li, H. Doucet, Adv. Synth. Catal. 355 (2013) 1423.
[7] (b) P.T. Anastas, J.C. Warner, Green Chemistry: Theory and Practice, Oxford University Press, New York, 1998, p. 30;
(b) T. Welton, Chem. Rev. 99 (1999) 2071;
(c) P.T. Anastas, M.M. Kirchhoff, Acc. Chem. Res. 35 (2002) 686.
[8] C. Fischmeister, H. Doucet, Green Chem. 13 (2011) 741.
[9] (a) G.L. Turner, J.A. Morris, M.F. Greaney, Angew. Chem., Int. Ed. 46 (2007) 7996;
(b) S.A. Ohnmacht, P. Mamone, A.J. Culshaw, M.F. Greaney, Chem. Commun. (2008) 1241;
(c) E. Ferrer Flegeau, M.E. Popkin, M.F. Greaney, Org. Lett. 10 (2008) 2717;
(d) S.A. Ohnmacht, A.J. Culshaw, M.F. Greaney, Org. Lett. 12 (2010) 224;
(e) L. Joucla, N. Batail, L. Djakovitch, Adv. Synth. Catal. (2010) 352;
(f) Y.-X. Su, Y.-H. Deng, T.-T. Ma, Y.-Y. Li, L.-P. Sun, Green Chem. 14 (2012) 1979;
(g) G. Park, S. Lee, S.J. Son, S. Shin, Green Chem. 15 (2013) 3468.
[10] (a) O. René, K. Fagnou, Org. Lett. 12 (2010) 2116;
(b) L. Ackermann, R. Vicente, Org. Lett. 11 (2009) 4922.
[11] (a) J. Roger, C. Verrier, R. Le Goff, C. Hoarau, H. Doucet, ChemSusChem 2 (2009) 951;
(b) J.J. Dong, J. Roger, C. Verrier, T. Martin, R. Le Goff, C. Hoarau, H. Doucet, Green Chem. 12 (2010) 2053;

(c) S. Bensaid, N. Laidaoui, D. El Abed, S. Kacimi, H. Doucet, Tetrahedron Lett. 52 (2011) 138;
(d) K. Beydoun, H. Doucet, ChemSusChem 4 (2011) 526;
(e) S. Bensaid, H. Doucet, ChemSusChem 5 (2012) 1559.
[12] (a) P. Arockiam, V. Poirier, C. Fischmeister, C. Bruneau, P.-H. Dixneuf, Green Chem. 11 (2009) 1871;
(b) P. Arockiam, C. Fischmeister, C. Bruneau, P.-H. Dixneuf, Angew. Chem. Int. Ed. 49 (2010) 6629;
(c) L.A. Adrio, J. Gimeno, C. Vicent, Chem. Commun. 49 (2013) 8320.
[13] K. Tanaka, Solvent-free organic synthesis, Wiley-VCH Verlag GmbH & Co., Weinheim, Germany, 2003.
[14] R.B. Bedford, C.J. Mitchell, R.L. Webster, Chem. Commun. 46 (2010) 3095.
[15] R.K. Henderson, C. Jiménez-González, D.J.C. Constable, S.R. Alston, G.G.A. Inglis, G. Fisher, J. Sherwood, S.P. Binks, A.D. Curzons, Green Chem. 13 (2011) 854.
[16] K. Watanabe, N. Yamagiwa, Y. Torisawa, Org. Proc. Res. Dev. 11 (2007) 251.
[17] (a) P. Tundo, M. Selva, Acc. Chem. Res. 35 (2002) 706;
(b) T. Sakakura, K. Kohno, Chem. Commun. (2009) 1312;
(c) B. Schäffner, F. Schäffner, S.P. Verevkin, A. Börner, Chem. Rev. 110 (2010) 4554;
(d) P.T. Anastas, W. Leitner, P.G. Jessop, C.J. Li, P. Wasserscheid, A. Stark, Handbook of Green Chemistry –Green Solvents, Wiley VCH, 2010.
[18] H.Y. Fu, L. Chen, H. Doucet, J. Org. Chem. 77 (2012) 4473.
[19] T. Cantat, E. Génin, C. Giroud, G. Meyer, A. Jutand, J. Organomet. Chem. 687 (2003) 365.
[20] (a) F. Pozgan, J. Roger, H. Doucet, ChemSusChem 1 (2008) 404;
(b) A. Battace, M. Lemhadri, T. Zair, H. Doucet, M. Santelli, Organometallics 26 (2007) 472;
(c) L. Zhao, C. Bruneau, H. Doucet, ChemCatChem 5 (2013) 255.