Organic &
Biomolecular
Chemistry

Cite this: *Org. Biomol. Chem.*, 2011, **9**, 8233

www.rsc.org/obc

COMMUNICATION

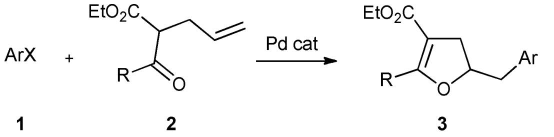
Functionalized 2,3-dihydrofurans *via* palladium-catalyzed oxyarylation of α-allyl-β-ketoesters†‡§

Sandro Cacchi,*[a] Giancarlo Fabrizi,[a] Antonella Goggiamani,[a] Antonia Iazzetti,[a] David Madec,[b] Giovanni Poli[c] and Guillaume Prestat[c]

Received 19th September 2011, Accepted 14th October 2011
DOI: 10.1039/c1ob06593a

The palladium-catalyzed reaction of (hetero)aryl bromides, chlorides, and nonaflates with α-allyl-β-ketoesters provides ready efficient access to functionalized 2,3-dihydrofurans. The reaction tolerates several useful substituents including chloro, fluoro, ether, ketone, ester, cyano, and nitro groups.

The 2,3-dihydrofuran motif is displayed in a large number of bioactive natural products as well as pharmaceutically important unnatural compounds such as neo-clerodane diterpenoids[1] and aflatoxin B1.[2] In addition, 2,3-dihydrofuran derivatives are useful synthetic intermediates.[3] Some of the most convenient approaches to the construction of the 2,3-dihydrofuran ring system are based on the reaction of active methylene compounds[4] or ylides[5] with suitable electrophiles. Functionalized 2,3-dihydrofuran rings have also been formed *via* reaction of active methylene compounds with olefins in the presence of manganese(III)acetate[6] or cerium(IV) ammonium nitrate[7] and by treating diazo compounds with olefins in the presence of copper-[8] or rhodium[9] catalysts. Palladium catalysis has also found its place in this field.[10] Nevertheless, despite the number of methods developed, the search for more general and versatile synthetic approaches to this class of compounds continues to be an active area of research thus justifying efforts to develop more general and versatile procedures, particularly when these procedures accommodate considerable functionalities and use readily available starting materials. Here we report such a method allowing for ready access to functionalized 2,3-dihydrofurans **3** through the palladium-catalyzed oxyarylation of α-allyl-β-ketoesters **2** (Scheme 1). Related chemistry has been recently reported by J. N. Kim *et al.*[11] who described the construction of 2,3-dihydrofuran rings incorporated into dihydroindenofuran scaffolds through the intramolecular oxyarylation of substrates that contain both the enolate precursor and a bromobenzene fragment in the same molecule.



Scheme 1 Palladium-catalyzed oxyarylation of α-allyl-β-ketoesters with aryl halides.

Using the reaction of 3-bromoanisole with ethyl 2-allyl-3-oxobutanoate **2a** as a probe for evaluating the reaction conditions, we initiated our study by examining the influence of ligands, bases, and solvents in the presence of $Pd_2(dba)_3$ at 100 °C in 0.08 M solutions. Low to moderate yields of **3a** were obtained using Cs_2CO_3 and XantPhos[12,13] in 1,4-dioxane by increasing the catalyst loading from 0.01 to 0.025 equiv (Table 1, entries 1–7). With dppf[13] or dppb[13] ligands or in the presence of $Pd(PPh_3)_4$ no evidence of **3a** was obtained and the Mizoroki–Heck derivative **4a** was isolated as the main product (Table 1, entries 8–10). A 52% yield of **3a** was isolated with SPhos,[13,14] but **4a** still formed in significant amounts (Table 1, entry 11). Substituting K_3PO_4 for Cs_2CO_3 led to a lower yield and lower *oxypalladation/Mizoroki–Heck reaction* selectivity (Table 1, entry 12). Pleasingly, an increase of both the yield and the *oxypalladation/Mizoroki–Heck reaction* selectivity were observed by switching to RuPhos[13,15] (Table 1, entry 13). Higher yield and selectivity were observed using MeCN as solvent (Table 1, entry 14) whereas toluene and DMF gave unsatisfactory results (Table 1, entries 15 and 16). Further optimization studies revealed that the best results could be obtained by using 0.025 equiv $Pd_2(dba)_3$, 0.05 equiv RuPhos, and 1.2 equiv Cs_2CO_3 in a more concentrated 0.25 M MeCN solution at 100 °C. Under these conditions, **3a** was isolated in 79% yield in 2.5 h and no Mizoroki–Heck product was observed (Table 1, entry 17). Cs_2CO_3 proved superior to other bases such as K_3PO_4, K_2CO_3, and $NaHCO_3$ (Table 1, entries 18–20).

However, when 4-bromoanisole, a model of electron-rich aryl bromides, was treated with **2a** under the best conditions found for 3-bromoanisole, a longer reaction time was required (very

---

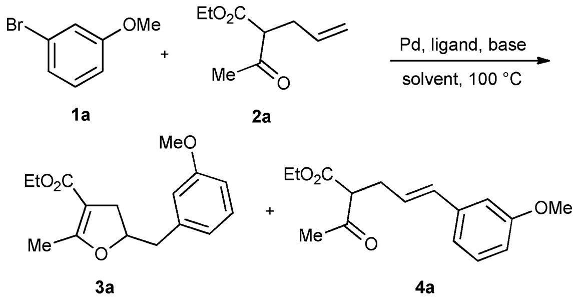
[a] *Dipartimento di Chimica e Tecnologie del Farmaco, Sapienza, Università di Roma, P.le A. Moro 5, 00185 Roma, Italy. E-mail: sandro.cacchi@uniroma1.it; Fax: +39 (06) 4991 2780; Tel: +39 (06) 4991 2795*
[b] *Université de Toulouse, UPS, LHFA, bât. 2R1, 118 route de Narbonne, 31062 Toulouse. CNRS, LHFA UMR 5069, 31062 Toulouse, France. E-mail: madec@chimie.ups-tlse.fr; Tel: +33 5 61 55 62 87*
[c] *UPMC Univ Paris 06, Institut Parisien de Chimie Moléculaire (UMR CNRS 7201), FR 2769, C. 183, 4 Place Jussieu, 75005 Paris, France. E-mail: giovanni.poli@upmc.fr; Tel: +33 1 44 27 55 72*

† This article is dedicated to Professor Alfredo Ricci on the occasion of his retirement.

‡ This work is the fruit of a collaborative project from COST, Action D40 "Innovative Catalysis: New Processes and Selectivities".

§ Electronic supplementary information (ESI) available: A complete description of experimental details and product characterization. See DOI: 10.1039/c1ob06593a

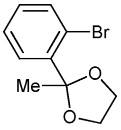
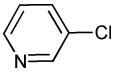
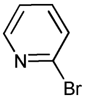
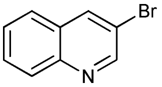
Table 1 The influence of ligands, solvents, and bases on the reaction of 3-methoxybromobenzene **1a** with ethyl 2-allyl-3-oxobutanoate **2a**[a]



Entry	Ligand or catalyst system (equiv)	Base	Solvent	Time (h)	Yield%[b] 3a	4a
1	XantPhos (0.02)	Cs_2CO_3	1,4-dioxane	5	20[c]	—
2	XantPhos (0.03)	Cs_2CO_3	1,4-dioxane	5.5	27[c]	—
3	XantPhos (0.03)	Cs_2CO_3	1,4-dioxane	3.5	25[d]	—
4	XantPhos (0.03)	Cs_2CO_3	1,4-dioxane	5.5	27[d,e]	—
5	XantPhos (0.03)	Cs_2CO_3	1,4-dioxane	8	24[d,f]	—
6	XantPhos (0.05)	Cs_2CO_3	1,4-dioxane	3	31[g]	—
7	XantPhos (0.05)	Cs_2CO_3	1,4-dioxane	3	23[g,h]	—
8	dppf (0.05)	Cs_2CO_3	1,4-dioxane	2.5	—[g]	60
9	dppb (0.05)	Cs_2CO_3	1,4-dioxane	6	—[g]	65
10	$Pd(PPh_3)_4$ (0.05)	Cs_2CO_3	1,4-dioxane	3	—	30
11	SPhos (0.05)	Cs_2CO_3	1,4-dioxane	22	52[g]	28
12	SPhos (0.05)	K_3PO_4	1,4-dioxane	24	32[g]	28
13	RuPhos (0.05)	Cs_2CO_3	1,4-dioxane	2.5	65[g]	13
14	RuPhos (0.05)	Cs_2CO_3	MeCN	2.5	74[g]	—
15	RuPhos (0.05)	Cs_2CO_3	toluene	1	44[g]	25
16	RuPhos (0.05)	Cs_2CO_3	DMF	1.5	55[g]	—
17	RuPhos (0.05)	Cs_2CO_3	MeCN	2.5	79[g,e]	—
18	RuPhos (0.05)	K_3PO_4	MeCN	1	60[e,g]	8
19	RuPhos (0.05)	K_2CO_3	MeCN	2	55[e,g]	—
20	RuPhos (0.05)	$NaHCO_3$	MeCN	9	traces[e,g,i]	—

[a] Unless otherwise stated, reactions were carried out on a 0.5 mmol scale at 100 °C in a 0.08 M solution, under a nitrogen atmosphere, using 1 equiv of **1a**, 1.2 equiv of **2a**, and 1.2 equiv of base. [b] Yields are given for isolated products. [c] 0.01 equiv $Pd_2(dba)_3$. [d] 0.015 equiv $Pd_2(dba)_3$. [e] 0.25 M. [f] 0.05 M. [g] 0.025 equiv $Pd_2(dba)_3$. [h] 1 equiv of **1a**, 2 equiv of **2a**. [i] **2a** was recovered in 52% yield.

Table 2 Synthesis of functionalized 2,3-dihydrofurans **3** from ethyl 2-allyl-3-oxobutanoate **2a**[a]

Entry	Aryl and heteroaryl halide **1**	Time (h)	Yield%[b] **3**		**4**	
1	3-$MeOC_6H_4Br$	2.5	79	**3a**	traces	**4a**
2	4-$MeOC_6H_4Br$	7	44	**3b**	8	**4b**
3		4.5	64[c]	**3b**	15	**4c**
4	4-$MeOC_6H_4Cl$	3.5	57[c]	**3b**	—	
5	4-$Me_2NC_6H_4Br$	5	33[c]	**3c**	28	**4c**
6	3-MeC_6H_4Br	7	65	**3d**	—	
7		5	79[c]	**3d**	—	
8	4-MeC_6H_4Br	24	54	**3e**	7	
9		4.5	73[c]	**3e**	—	
10	2-MeC_6H_4Br	2	70[c]	**3f**	—	
11			—	—	—	
12	PhBr	2	95	**3g**	—	
13	4-PhC_6H_4Br	1.5	82	**3h**	—	
14	4-PhC_6H_4ONf	0.5	71	**3h**	—	
15	4-FC_6H_4Br	5	70	**3i**	—	
16	3-$F_3CC_6H_4Br$	2.5	92	**3j**	—	
17	3-$F_3CC_6H_4Cl$	5.5	94	**3j**	—	
18	4-ClC_6H_4Br	3	66	**3k**	—	
19	4-$EtO_2CC_6H_4Br$	1.25	91	**3l**	—	
20	4-$MeCOC_6H_4Br$	1	91	**3m**	—	
21	4-NCC_6H_4Br	1.25	86	**3n**	traces	**4n**
22	2-NCC_6H_4Br	2.5	92	**3o**	—	
23	3-$O_2NC_6H_4Br$	4.5	81	**3p**	—	
24		24	37	**3q**	—	
25		2.5	57[c]	**3q**	—	
26		5.5	51	**3r**	—	
27		0.75	74[c]	**3r**	—	
28		2.25	75	**3s**	7	**4s**

[a] Unless otherwise stated, reactions were carried out on a 0.5 mmol scale, in a 0.25 M MeCN solution, under a nitrogen atmosphere at 100 °C, using 1 equiv of **1**, 1.2 equiv of **2a**, 1.2 equiv of Cs_2CO_3, 0.025 equiv of $Pd_2(dba)_3$, and 0.05 equiv of RuPhos. [b] Yields are given for isolated products. [c] 0.1 equiv RuPhos.

likely because of the slower, rate determining oxidative addition step), early formation of palladium black was observed, and the corresponding 2,3-dihydrofuran derivative **3b** was isolated only in 44% yield. The amount of RuPhos was then increased to 0.1 equiv to favor the solubilization of the palladium catalyst. To our delight, the desired dihydrofuran derivative was isolated in a satisfactory 64% yield (Table 2, entry 3). Consequently, we decided to employ 0.05 equiv RuPhos with neutral or electron-poor aryl halides and 0.1 equiv RuPhos with electron-rich aryl halides.

Using these conditions, we next explored the scope and generality of the process (Table 2). In general, clean formation of 2,3-dihydrofurans **3** was observed with a variety of neutral, electron-poor, and electron-rich aryl bromides. The reaction tolerates several useful substituents including chloro, fluoro, ether, ketone, ester, cyano, and nitro groups. The ability to incorporate the chloro substituent (Table 2, entry 18) is particularly interesting since it can be used for further synthetic manipulations *via* transition metal-catalyzed coupling reactions. Only 4-bromo-*N*,*N*-dimethylaniline, among the aryl bromides investigated, provided the corresponding 2,3-dihydrofuran in low yield along with significant amounts of the Heck product (Table 2, entry 5). Ortho substituents such as *o*-methyl and *o*-cyano groups (Table 2, entries 10 and 22, respectively) are also well tolerated. However, a bulkier *o*-ketal aryl bromide failed to give the desired 2,3-dihydrofuran derivative (Table 2, entry 11).

The method can be extended to aryl nonaflates (Table 2, entry 14) and chlorides, although electron-poor aryl chlorides afford oxyarylation products in excellent yields (Table 2, entry 17) whereas electron-rich aryl chlorides are less successful substrates (Table 2, entry 4).

Table 3 The reaction of aryl halides **1** with α-allyl-β-ketoesters **2**[a]

Entry	Aryl halide **1**	α-Allyl-β-ketoesters **2** R	Time (h)	Yield%[b]			
				3		**4**	
1	4-NCC_6H_4Br	2-furyl	0.66	84	**3t**	—	
2	4-MeC_6H_4Br	2-furyl	2.5	75[c]	**3u**	—	
3	4-NCC_6H_4Br	Ph	7	46	**3v**	—	
4	4-NCC_6H_4Br	Ph	2.5	84[c,d]	**3v**	—	**4v**
5	4-MeC_6H_4Br	Ph	21	traces	**3w**	10	**4w**
6	4-MeC_6H_4Br	Ph	24	traces[c]	**3w**	10	**4w**
7	4-MeC_6H_4Br	Ph	4	66[e]	**3w**	15	**4w**
8	4-NCC_6H_4Br	4-MeC_6H_4	1.25	69[c]	**3x**	—	
9	4-MeC_6H_4Br	4-MeC_6H_4	5.25	70[c]	**3y**	traces	**4y**
10	4-NCC_6H_4Br	4-$MeOC_6H_4$	1	51[c]	**3z**	—	
11	4-MeC_6H_4Br	4-$MeOC_6H_4$	2.5	52[c]	**3za**	—	
12	4-NCC_6H_4Br	4-$O_2NC_6H_4$	24	23	**3zb**	—	
13	4-MeC_6H_4Br	4-$O_2NC_6H_4$	24	11[c]	**3zc**	16	**4zc**
14	4-NCC_6H_4Br	*i*-Pr	0.75	90	**3zd**	traces	**4zd**
15	4-MeC_6H_4Br	*i*-Pr	2.5	83[c]	**3ze**	—	
16	4-NCC_6H_4Br	*t*-Bu	46	—	—	—	
17	4-MeC_6H_4Br	*t*-Bu	22	10[c]	**3zf**	38	**4zf**

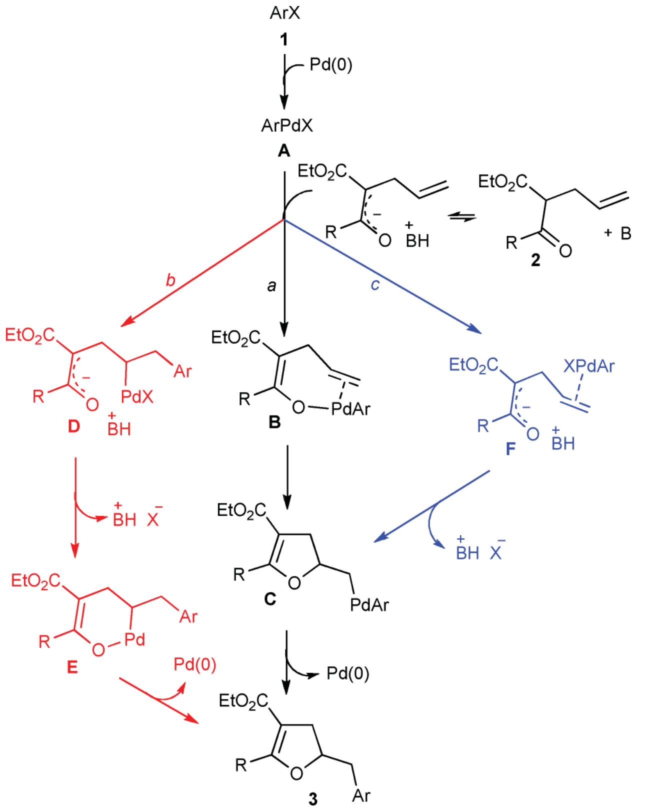
[a] Unless otherwise stated, reactions were carried out on a 0.33 mmol scale, in a 0.25 M MeCN solution, under a nitrogen atmosphere at 100 °C, using 1 equiv of **1**, 1.2 equiv of **2**, 1.2 equiv of Cs_2CO_3, 0.025 equiv of $Pd_2(dba)_3$, and 0.05 equiv of RuPhos. [b] Yields are given for isolated products. [c] 0.1 equiv RuPhos. [d] At 110° C. [e] 0.15 equiv Ruphos.

Heterocyclic halides were briefly investigated and were found to give the corresponding 2,3-dihydrofurans in moderate to high yields (Table 2, entries 24–28).

The influence of the substituent diversity of the α-allyl-β-ketoesters **2** was also explored. Our preparative results are summarized in Table 3. Although we did not make a systematic study and generalization from these results have to be drawn with caution, nevertheless some basic trends can be recognized; *i.e.*, the oxyarylation reaction appear to be disfavored by substituents decreasing the nucleophilicity of the enolate of the β-ketoester both with electron-rich (Table 3, entry 13) and electron-poor (Table 3, entry 12) aryl halides. Even the presence of bulky R substituents has a detrimental effect on the reaction outcome (Table 3, entries 16 and 17).

Most probably the reaction proceeds according to a mechanism analogous to that described for related palladium-catalyzed reactions[16] (Scheme 2, path *a*; ligands are omitted for clarity's sake). The oxidative addition of the aryl halide to Pd(0) would generate the σ-arylpalladium complex **A**, which could undergo an oxygen displacement with the *in situ* generated enolate to afford the adduct **B**. A subsequent intramolecular oxypalladiation would provide the intermediate **C** from which the 2,3-dihydrofuran derivative would form *via* reductive elimination. However, the alternative catalytic cycle involving the intermediacy of the carbopalladation complex **D**, which would generate the palladacycle **E** and then the 2,3-dihydrofuran product *via* reductive elimination (Scheme 2, path *b*) or that proceeding through an intramolecular nucleophilic attack of the oxygen on the olefinic moiety activated by a σ-arylpalladium complex (Scheme 2, path *c*) cannot be ruled out.

In conclusion, an efficient palladium-catalyzed oxyarylation approach to 2,3-dihydrofurans from readily available α-allyl-β-ketoesters has been developed. The procedure is simple and provides the desired products in good to excellent yields. Aryl bromides and chlorides as well as heteroaryl halides can be used in this chemistry. The new method tolerates several useful substituents including chloro, fluoro, ether, ketone, ester, cyano, and nitro groups.



Scheme 2 Proposed mechanism for the palladium-catalyzed synthesis of functionalized 2,3-dihydrofurans from aryl halides and α-allyl-β-ketoesters.

Notes and references

1. For a review, see: J. Coll and Y. A. Tandrón, *Phytochemistry Rev.*, 2008, **7**, 25.
2. (*a*) J.-Y. Lallemand, Y. Six and L. Ricard, *Eur. J. Org. Chem.*, 2002, 503; (*b*) G. N. Krishna Kumari, J. Balachandran, S. Aravind and M. R. Ganesh, *J. Agric. Food Chem.*, 2003, **51**, 1555; (*c*) S. Rosselli, A. Maggio, F. Piozzi and M. Bruno, *Tetrahedron*, 2004, **60**, 8791.
3. R. Zhang, Y. Liang, G. Zhou, K. Wang and D. Dong, *J. Org. Chem.*, 2008, **73**, 8089.
4. For recent, selected references, see: (*a*) R. Antonioletti, G. Righi, L. Oliverim and P. Bovicelli, *Tetrahedron Lett.*, 2000, **41**, 10127; (*b*) M. A. Calter and C. Zhu, *Org. Lett.*, 2002, **4**, 205; (*c*) M. A. Calter, C. Zhu and R. J. Lachicotte, *Org. Lett.*, 2002, **4**, 209; (*d*) R. Antonioletti, P. Bovicelli and S. Malancona, *Tetrahedron*, 2002, **58**, 589; (*e*) V. Calò, F. Scordari, A. Nacci, E. Schingaro, L. D'Accolti and A. Monopoli, *J. Org. Chem.*, 2003, **68**, 4406; (*f*) E. Tang, X. Huang and W. M. Xu, *Tetrahedron*, 2004, **60**, 9963; (*g*) C. Xing and S. Zhu, *J. Org. Chem.*, 2004, **69**, 6486; (*h*) M. A. Calter, R. M. Phillips and C. Flaschenriem, *J. Am. Chem. Soc.*, 2005, **127**, 14566; (*i*) J. Ying, L. X. Ying, J. Lin, H. Wei, S. X. Li and Z. S. Yong, *Chirality*, 2007, **19**, 386; (*j*) S. Kitagaki, D. Shibata and C. Mukai, *Tetrahedron Lett.*, 2007, **48**, 1735; (*k*) B. C. Ranu, L. Adak and S. Banerjee, *Tetrahedron Lett.*, 2008, **49**, 4613; (*l*) C. P. Chuang and A. I. Tsai, *Tetrahedron*, 2008, **64**, 7511; (*m*) A. M. Maharramov, N. D. Sadikhova, I. G. Mammadov and M. A. Allahverdiyev, *Chem. Heterocyclic Comp.*, 2009, **45**, 400; (*n*) M. Adamo, S. Suresh and L. Piras, *Tetrahedron*, 2009, **65**, 5402; (*o*) D. P. Sahu, S. K. Giri, V. Varshney and S. Kumar, *Synth. Commun.*, 2009, **39**, 3406; (*p*) B. M. Vinosha, S. Renuga, M. Gnanadeebam, S. Perumal and A. Lycka, *Synth. Commun.*, 2009, **39**, 2776; (*q*) C. Zhong, T. Liao, O. Tuguldur and X. Shi, *Org. Lett.*, 2010, **12**, 2064.
5. For recent, selected references, see: *sulfonium ylides*: (*a*) Y. Jiang and D. Ma, *Tetrahedron: Asymmetry*, 2002, **13**, 1033; (*b*) X. L. Sun and Y. Tang, *Acc. Chem. Res.*, 2008, **41**, 937; *phosphonium ylides*: (*c*) W. Cao, W. Ding, J. Chen, Y. Chen, Q. Zang and G. Chen, *Synth. Commun.*, 2004, **34**, 1599; (*d*) S. Redon, S. Leleu, X. Pannecoucke, X. Franck and F. Outurquin, *Tetrahedron*, 2008, **64**, 9293; *arsonium ylides*: (*e*) J. Qian, W. Cao, H. Zhang, J. Chen and S. Zhu, *J. Fluorine Chem.*, 2007, **128**, 207; (*f*) W. Cao, H. Zhang, J. Chen, X. Zhou, M. Shao and M. C. McMills, *Tetrahedron*, 2008, **64**, 163; *ammonium ylides*: (*g*) Z. Yang, M. Fan, R. Mu, W. Liu and Y. Liang, *Tetrahedron*, 2005, **61**, 9140; (*h*) M. Fan, Z. Yan, W. Liu and Y. Liang, *J. Org. Chem.*, 2005, **70**, 8204; (*i*) M. Fan, L. Guo, X. Liu, W. Liu and Y. Liang, *Synthesis*, 2005, 391; (*j*) Q.-F. Wang, H. Hou, L. Hui and C.-G. Yan, *J. Org. Chem.*, 2009, **74**, 7403.
6. For recent, selected references, see: (*a*) F. Garzino F., A. Meou and P. Brun, *Tetrahedron Lett.*, 2000, **41**, 9803; (*b*) G. Bar, A. F. Parsons and C. B. Thomas, *Tetrahedron Lett.*, 2000, **41**, 7751; (*c*) F. Garzino, A. Méou and P. Brun, *Tetrahedron Lett.*, 2002, **43**, 5049; (*d*) R. Calískan, T. Pekel, W. H. Watsonc and M. Balci, *Tetrahedron Lett.*, 2005, **46**, 6227; (*e*) M. Yılmaz, N. Uzunalioglu and A. T. Pekel, *Tetrahedron*, 2005, **61**, 8860; (*f*) E. V. Burgaz, M. Yilmaz, A. T. Pekel and A. Oktemer, *Tetrahedron*, 2007, **63**, 7229; (*g*) G. W. Wang, Y. W. Dong, P. Wu, T. T. Yuan and Y. B. Shen, *J. Org. Chem.*, 2008, **73**, 7088; (*h*) E. Findik, A. Dingil, I. Karaman, Y. Budak and M. Ceylan, *E-J. Chem.*, 2009, **6**(S1), S53.
7. For recent, selected references, see: (*a*) Y. R. Lee, B. S. Kim and D. H. Kim, *Tetrahedron*, 2000, **56**, 8845; (*b*) K. Kobayashi, K. Nagase, O. Morikawa and H Konishi, *Heterocycles*, 2003, **60**, 939; (*c*) Y. Zhang, A. J. Raines and R. A. Flowers, *Org. Lett.*, 2003, **5**, 2363.
8. For recent, selected references, see: (*a*) O. Anaç, A. D. Özdemir and Ö. Sezer, *Helv. Chim. Acta*, 2003, **86**, 290; (*b*) S. Son and G. C. Fu, *J. Am. Chem. Soc.*, 2007, **129**, 1046; (*c*) O. Anaç, Ö. Sezer, Ö. Candan, F. S. Güngör and M. S. Cansever, *Tetrahedron Lett.*, 2008, **49**, 1062; (*d*) F. S. Güngör, O. Anaç and Ö. Sezer, *Tetrahedron Lett.*, 2007, **48**, 4883.
9. (*a*) Y. R. Lee and J. Y. Suk, *Tetrahedron*, 2002, **58**, 2359; (*b*) Y. R. Lee and J. C. Hwang, *Eur. J. Org. Chem.*, 2005, 1568.
10. For recent, selected references, see: (*a*) S. Ma, Z. Zheng and X. Jiang, *Org. Lett.*, 2007, **9**, 529; (*b*) R. Shen and X. Huang, *Org. Lett.*, 2008, **10**, 3283; (*c*) B. Alcaide, P. Almendros, T. M. del Campo and R. Carrascosa, *Chem.–Asian J.*, 2008, **3**, 1140; (*d*) R. Shen, S. Zhu and X. Huang, *J. Org. Chem.*, 2009, **74**, 4118; (*e*) R. W. Shen, S. G. Zhu, Q. Q. Xia, L. L. Wu and X. Huang, *Chinese Chem. Lett.*, 2009, **20**, 165; (*f*) V. Stonkus, K. Edolfa, L. Leite, J. W. Sobczak, L. Plyasova and P. Petrova, *Appl. Catal. A-Gen.*, 2009, **362**, 147; (*g*) W. Shu and S. Ma, *Tetrahedron*, 2010, **66**, 2869; (*h*) S. Lin, G.-L. Zhao, L. Deiana, J. Sun, Q. Zhang, H. Leijonmarck and A. Córdova, *Chem.–Eur. J.*, 2010, **16**, 13930.
11. E. S. Kim, K. H. Kim, S. Park and J. N. Kim, *Tetrahedron Lett.*, 2010, **51**, 4648.
12. M. Kranenburg, Y. E. M. van der Burgt, P. C. J. Kamer, P. W. N. M. van Leeuwen, K. Goubitz and J. Fraanje, *Organometallics*, 1995, **14**, 3081.
13. XantPhos = 9,9-dimethyl-4,5-bis(diphenylphosphino)xanthene; SPhos = 2-(2′,6′-dimethoxybiphenyl)dicyclohexylphosphine; dppf = 1,1′-bis(diphenylphosphino)ferrocene; dppb = 1,3-bis(diphenylphosphino)butane; RuPhos = 2-(2′,6′-diisopropoxybiphenyl)-dicyclohexylphosphine.
14. T. E. Barder, S. D. Walker, J. R. Martinelli and S. L. Buchwald, *J. Am. Chem. Soc.*, 2005, **127**, 4685.
15. J. E. Milne and S. L. Buchwald, *J. Am. Chem. Soc.*, 2004, **126**, 13028.
16. (*a*) J. P. Wolfe and M. A. Rossi, *J. Am. Chem. Soc.*, 2004, **126**, 1620; (*b*) M. B. Hay and J. P. Wolfe, *J. Am. Chem. Soc.*, 2005, **127**, 16468; (*c*) M. B. Hay, A. R. Hardin and J. P. Wolfe, *J. Org. Chem.*, 2005, **70**, 3099; (*d*) M. B. Hay and J. P. Wolfe, *Tetrahedron Lett.*, 2006, **47**, 2793; (*e*) J. S. Nakhla, J. W. Kampf and J. P. Wolfe, *J. Am. Chem. Soc.*, 2006, **128**, 2893.