Organic & Biomolecular Chemistry

Dynamic Article Links

Cite this: *Org. Biomol. Chem.*, 2011, **9**, 1727

www.rsc.org/obc

COMMUNICATION

Heck reaction of arenediazonium salts with *N*,*N*-diprotected allylamines. Synthesis of cinnamylamines and indoles†

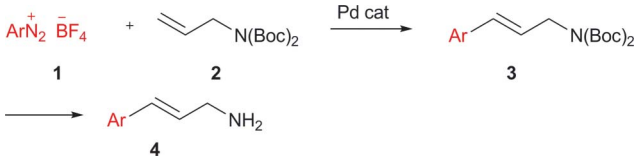
Sandro Cacchi,* Giancarlo Fabrizi, Antonella Goggiamani and Alessio Sferrazza

Received 19th November 2010, Accepted 19th January 2011
DOI: 10.1039/c0ob01052a

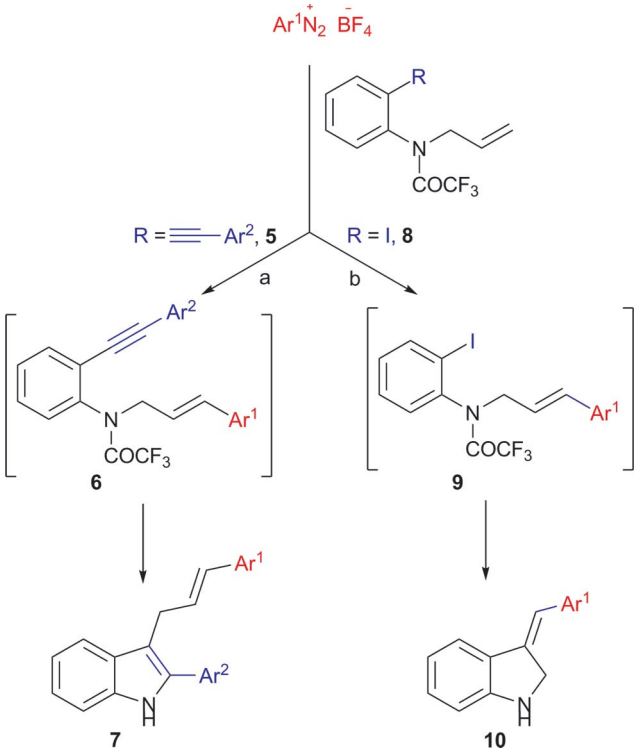
Novel palladium-catalyzed reactions of arenediazonium tetrafluoroborates with *N*,*N*-diprotected allylamines are presented. The reaction of arenediazonium tetrafluoroborates with *N*,*N*-(Boc)$_2$ allylamine allows for an easy approach to cinnamylamines whereas using 2-alkynyl-*N*-(allyl)-trifluoroacetanilides and 2-iodo-*N*-(allyl)trifluoroacetanilide the reaction provides a useful tool for appending indole rings to aniline fragments.

Because of their importance as synthetic intermediates[1] and as functional groups in many biologically active compounds,[2] considerable effort has been directed toward the development of methodologies for the synthesis of primary allylic amines.[3] Palladium catalysis has provided some of the most efficient procedures, typically *via* amination of allylic esters[3a,4] or alcohols,[5] allylic C–H amination,[6] aza-Claisen rearrangement,[7] and Heck reaction of allylamine derivatives.[1f,3a,8] As to the latter, reactions have been usually performed with aryl halides or triflates. However, although arenediazonium salts offer significant advantages over aryl halides and triflates (for example, they are less expensive and more reactive, react under milder conditions, Heck arylations can be carried out in air and omitting phosphine ligands) and despite their broad application in the Heck reaction,[9,10] no example using arenediazonium salts has been described.

Therefore, as part of our on-going research in palladium-catalyzed reactions of arenediazonium salts,[9j,k,11] it appeared of interest to us to investigate their involvement in a new approach to cinnamylamines *via* Heck reaction with the *N*,*N*-(Boc)$_2$ allylamine **2** (Scheme 1). Our planning also included the application of this chemistry to allylamines bearing functional groups able to undergo a subsequent cyclization reaction. In particular, we considered that the reaction of 2-alkynyl-*N*-(allyl)trifluoroacetanilides **5** with arenediazonium salts would lead to 2,3-disubstituted indoles **7**[12] through a sequential Heck reaction/aminopalladation/reductive elimination process[13] (Scheme 2a). Furthermore, 2-iodo-*N*-(allyl)trifluoroacetanilides **8** would afford alkylidene indolines **10** (Scheme 2b).



Scheme 1 Synthesis of cinnamylamines from arenediazonium tetrafluoroborates and *N*,*N*-(Boc)$_2$ allylamine.



Scheme 2 Synthesis of indole derivatives from arenediazonium tetrafluoroborates and 2-alkynyl-*N*-(allyl)trifluoroacetanilides **5** or 2-iodo-*N*-(allyl)trifluoroacetanilides **8**.

We started our study by examining the reaction of **2** with 4-methoxydiazobenzene tetrafluoroborate **1a**, a model of electron-rich arenediazonium salts. After an initial screening of solvents, bases, temperature, and precursors of Pd(0), we found that the use of 0.04 equiv of Pd$_2$(dba)$_3$ and 4.5 equiv of NaOAc, in MeCN at 35 °C produced **3a** after 0.5 h in 61% yield (Table 1, entry 5) along with a 24% yield of the γ,γ-diarylated derivative **11a**. Further

Dipartimento di Chimica e Tecnologie del Farmaco, La Sapienza, Università di Roma, P.le A. Moro 5, 00185 Rome, Italy. E-mail: sandro.cacchi@uniroma1.it; Fax: +39(06)4991-2780; Tel: +39(06)4991-2795

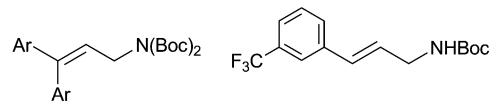
† Electronic supplementary information (ESI) available: A complete description of experimental details and product characterization. See DOI: 10.1039/c0ob01052a

Table 1 Optimization of the reaction of 4-methoxydiazobenzene tetrafluoroborate **1a** with *N*,*N*-(Boc)$_2$ allylamine **2**[a]

entry	**1a** : **2**	[Pd] (equiv)	base (equiv)	solvent	*T*/°C	time (h)	yield%[b] of **3a**
1	2 : 1	$Pd(OAc)_2$ (0.05)	—	MeOH	35	18	traces
2	2 : 1	$Pd(OAc)_2$ (0.05)	$CaCO_3$ (2)	MeOH	50	6	traces
3	2.1	$Pd(OAc)_2$ (0.05)	EtN(*i*-Pr)$_2$ (2)	MeOH	50	4	—[c]
4	1 : 1.1	$Pd(OAc)_2$ (0.05)	DABCO (3)	MeCN	rt	8	—
5	1.5 : 1	$Pd_2(dba)_3$ (0.04)	NaOAc (4.5)	MeCN	35	0.5	61[d]
6	1 : 1.1	$Pd_2(dba)_3$ (0.04)	NaOAc (3)	MeCN	rt	0.5	92
7	1 : 1.1	$Pd_2(dba)_3$ (0.02)	NaOAc (3)	MeCN	rt	3	90

[a] Reactions were carried out on a 0.5 mmol scale in 5 mL of solvent. [b] Yields are given for isolated products. [c] An almost quantitative reduction of **1a** to anisole was observed. [d] The γ,γ-diarylated derivative **11a** was isolated in 24% yield.

optimization of the reaction conditions led to the isolation of **3a** in 90% yield using 0.02 equiv of $Pd_2(dba)_3$ and 3 equiv of NaOAc at room temperature (Table 1, entry 7).‡



11a **12g**

Ar = 4-MeOC$_6$H$_4$

However, no vinylic substitution product formation was observed when these conditions were applied to 3-trifluoromethyldiazobenzene tetrafluoroborate **1g**, a model of electron-poor arenediazonium salts. Better results, although unsatisfactory from a synthetic point of view, were obtained omitting the base and using MeOH as the solvent. The corresponding vinylic substitution derivative **3g** was isolated in 35% yield after 5 h at room temperature. The main reaction product (59% yield) was the monoprotected vinylic substitution derivative **12g**, most probably formed by a partial deprotection process due to the acidity of the reaction medium.

We then came back to optimizing reaction conditions with electron-poor arenediazonium salts and found that the vinylic substitution derivative **3g** could be obtained in 83% yield in the presence of 0.02 equiv of $Pd_2(dba)_3$ and 1.5 equiv of $CaCO_3$ in MeOH[14] (3.5 h, room temperature). Nevertheless, these conditions proved less successful with electron-rich arenediazonium salts. Compound **1a** produced **3a** only in 65% yield after 4 h.

Therefore, two protocols were used when we next explored the scope and generality of the reaction: $Pd_2(dba)_3$, NaOAc, MeCN, room temperature with neutral and electron-rich arenediazonium salts (procedure A); $Pd_2(dba)_3$, $CaCO_3$, MeOH, room temperature with electron-poor arenediazonium salts (procedure B).

As shown by Table 2, vinylic substitution products **3** were isolated in good to excellent yields under these conditions and several useful functional groups are tolerated, including *ortho* as well as chloro, bromo, and iodo substituents. The ability to incorporate the latter makes this reaction particularly attractive for increasing the molecular complexity, for example *via* transition metal-catalyzed coupling reactions.

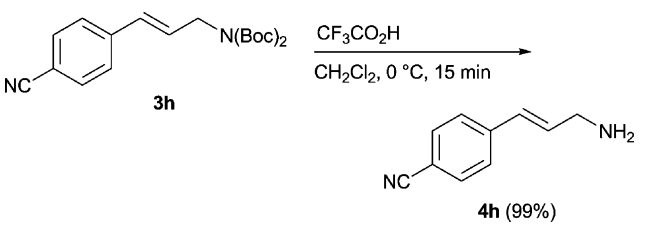
Compounds **3** can be readily converted into the corresponding cinnamylamines **4** as shown by the preparation of cinnamylamine **4h** from **3h** in almost quantitative yield (Scheme 3).

The synthesis of 2,3-disubstituted indoles **7** from the *N*,*N*-diprotected allylamine **5** involves a vinylic substitution step to give **6** followed by an intramolecular aminopalladation/reductive

Table 2 Palladium-catalyzed reaction of arenediazonium tetrafluoroborates **1** with *N*,*N*-(Boc)$_2$ allylamine **2**[a]

entry	**1**	proc	time (h)	yield%[b] of **3**	
1	4-MeOC$_6$H$_4$N$_2$BF$_4$	A	3	90	**3a**
2	2-MeOC$_6$H$_4$N$_2$BF$_4$	A	2	85	**3b**
3	2,4-Me$_2$C$_6$H$_3$N$_2$BF$_4$	A	5	83	**3c**
4	3,5-Me$_2$C$_6$H$_3$N$_2$BF$_4$	A	3	72	**3d**
5	2-PhC$_6$H$_4$N$_2$BF$_4$	A	3	61	**3e**
6	PhN$_2$BF$_4$	A	2.5	80	**3f**
7	3-CF$_3$C$_6$H$_4$N$_2$BF$_4$	B	3.5	83	**3g**
8	4-CNC$_6$H$_4$N$_2$BF$_4$	B	1.5	83	**3h**
9	4-MeCOC$_6$H$_4$N$_2$BF$_4$	B	5	70	**3i**
10	4-MeO$_2$CC$_6$H$_4$N$_2$BF$_4$	B	6	67	**3j**
11	2-ClC$_6$H$_4$N$_2$BF$_4$	B	4	83	**3k**
12	2-BrC$_6$H$_4$N$_2$BF$_4$	B	4	74	**3l**
13	4-IC$_6$H$_4$N$_2$BF$_4$	B	4	63	**3m**
14	4-BrC$_6$H$_4$N$_2$BF$_4$	B	3	63	**3n**
15	4-ClC$_6$H$_4$N$_2$BF$_4$	B	4	77	**3o**

[a] Reactions were carried out on a 0.5 mmol scale at room temperature using 1 equiv of **1**, 1.1 equiv of **2**, 0.02 equiv of $Pd_2(dba)_3$, and (procedure A) 3 equiv of NaOAc in 5 mL of MeCN or (procedure B) 1.5 equiv of $CaCO_3$ in 5 mL MeOH. [b] Yields are given for isolated products.



3h **4h** (99%)

Scheme 3 Typical procedure for the preparation of cinnamylamines from the corresponding *N*,*N*-(Boc)$_2$ precursors.

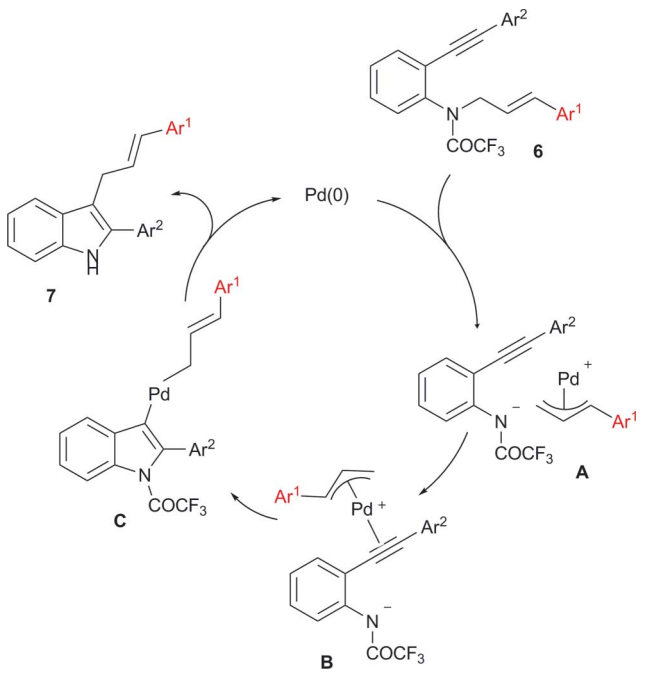
elimination step. It would help immensely if the Heck reaction/aminopalladation/reductive elimination sequence could be done without isolating the intermediates. Herein we report that this process can be performed through a one-pot protocol adding PPh_3 and K_2CO_3 to the crude mixture formed in the Heck reaction (when carried out in MeCN) or to the crude mixture formed in the first step after evaporating the volatile material (when carried out in MeOH) and increasing the temperature to 100 °C. Our preparative results are summarized in Table 3.

The mechanism of the aminopalladation/reductive elimination reaction most probably involves the basic steps outlined in Scheme 4. The reaction of Pd(0) with **6** affords the π-allylpalladium complex **A**, from which **B** is formed *via* coordination of the C–C triple bond to palladium. A subsequent intramolecular

Table 3 Synthesis of 2,3-disubstituted indoles **7** from arenediazonium tetrafluoroborates **1** and 2-alkynyl-*N*-(allyl)trifluoroacetanilides **5**[a]

entry	**1** Ar^1	**5** Ar^2	time (h)[b]	yield%[c] of **7**	
1	4-$MeOC_6H_4$	Ph	2 + 8	68	**7a**
2	4-$MeOC_6H_4$	4-$MeCOC_6H_4$	1 + 12	79	**7b**
3	4-$MeOC_6H_4$	2-ClC_6H_4	1 + 12	88	**7c**
4	Ph	Ph	0.5 + 12	83	**7d**
5	4-CNC_6H_4	4-$MeOC_6H_4$	2 + 12	69	**7e**
6	4-CNC_6H_4	4-ClC_6H_4	1 + 6	72	**7f**
7	4-CNC_6H_4	Ph	1 + 10	73	**7g**
8	4-CNC_6H_4	4-$MeCOC_6H_4$	1 + 12	73	**7h**

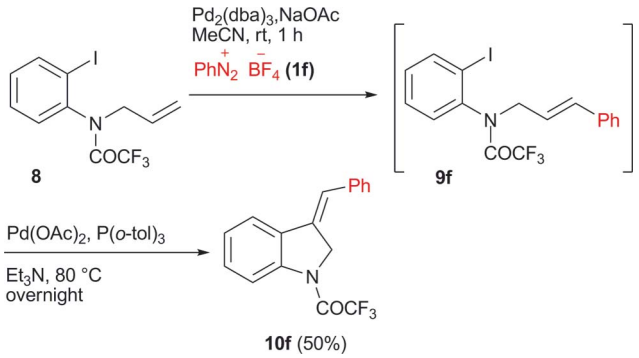
[a] Reactions were carried out on a 0.25 mmol scale under the following conditions: *first step*: room temperature, 1.1 equiv of **1**, 1 equiv of **5**, 0.02 equiv of $Pd_2(dba)_3$, and (procedure A) 3 equiv of NaOAc in 2.5 mL of MeCN or (procedure B) 1.5 equiv of $CaCO_3$ in 2.5 mL of MeOH; *second step*: 100 °C after the addition of 0.16 equiv of PPh_3 and 2 equiv of K_2CO_3 to the crude mixture formed in the first step (when carried out in MeCN) or to the crude mixture formed in the first step after evaporating the volatile material (when carried out in MeOH). [b] Reaction times refer to the first and to the second step, respectively. [c] Yields are given for isolated products.



Scheme 4 Proposed mechanism for the cyclization of **6** to 3-allylic 2-arylindoles.

aminopalladation reaction gives rise to the regioselective formation of **C** that undergoes a reductive elimination reaction to give **7** and regenerates the active palladium catalyst.

The potential of the Heck reaction of arenediazonium salts with *N*,*N*-disubstituted allylamines in appending indole moieties to aniline fragments is further demonstrated by the synthesis of alkylidene indolines from readily available 2-iodo-*N*-(allyl)trifluoroacetanilide **8**. As an example, we report that the reaction of **8** with **1f** followed by the intramolecular Heck reaction of the resultant **9f** affords the indoline **10f** in 50% overall yield (Scheme 5). **10f** was isolated as a single stereoisomer and its *Z* configuration was established by NOESY experiments. The synthesis has been performed as a one-pot process adding the



Scheme 5 Typical procedure for the preparation of alkylidene indoline from *o*-iodo-*N*-allyl-trifluoroacetanilide.

reagents required for the cyclization step to the crude mixture formed in the first step after evaporating the volatile material.

In conclusion, novel palladium-catalyzed reactions of arenediazonium tetrafluoroborates with *N*,*N*-diprotected allylamines have been developed. The reaction of arenediazonium tetrafluoroborates with *N*,*N*-$(Boc)_2$ allylamine allows for an easy approach to cinnamylamines. The new method tolerates a variety of useful functional groups, including *ortho* as well as chloro, bromo, and iodo substituents. With 2-alkynyl-*N*-(allyl)trifluoroacetanilides and 2-iodo-*N*-(allyl)trifluoroacetanilide the reaction provides an exceedingly useful tool for appending indole rings to aniline fragments.

Acknowledgements

We gratefully acknowledge GlaxoSmithKline for their generous financial support and a fellowship position and Dr Alcide Perboni and Paolo Stabile of GlaxoSmithKline for valuable discussions. We are also indebted to MURST and the University "La Sapienza" for financial support.

Notes and references

‡ No vinylic substitution derivative was formed after 8 h when the same reaction was carried out with free NH allylamine. Using *N*-Boc allylamine produced after 4 h a 57% yield of a regioisomeric mixture of monoarylated derivatives (γ-arylated : β-arylated = 3 : 1).

1 (*a*) J. Blid, O. Panknin, P. Tuzina and P. Somfai, *J. Org. Chem.*, 2007, **72**, 1294; (*b*) J. Jeon, M. Shin, J. W. Yoo, J. S. Oh, J. G. Bae, S. H. Jung and Y. G. Kim, *Tetrahedron Lett.*, 2007, **48**, 1105; (*c*) W. J. Bromley, M. Gibson, S. Lang, S. A. Raw, A. C. Whitwood and R. J. K. Taylor, *Tetrahedron*, 2007, **63**, 6004; (*d*) S. Mukherjee and B. List, *J. Am. Chem. Soc.*, 2007, **129**, 11336; (*e*) S. G. Davies, K. B. Ling, P. M. Roberts, A. J. Russell and J. E. Thomson, *Chem. Commun.*, 2007, 4029; (*f*) T. P. Ribelin, A. S. Judd, I. Akritopoulou-Zanze, R. F. Henry, J. L. Cross, D. N. Whittern and S. W. Djuric, *Org. Lett.*, 2007, **9**, 5119; (*g*) T. Jensen, H. Pedersen, B. Bang-Andersen, R. Madsen and M. Joergensen, *Angew. Chem., Int. Ed.*, 2008, **47**, 888; (*h*) B. Weiner, A. Baeza, T. Jerphagnon and B. L. Feringa, *J. Am. Chem. Soc.*, 2009, **131**, 9473; (*i*) R. M. Aranha, A. M. Bowser and J. S. Madalengoitia, *Org. Lett.*, 2009, **11**, 575; (*j*) T.-S. Jiang and J.-H. Li, *Chem. Commun.*, 2009, 7236; (*k*) M. L. Weinrich and H. P. Beck, *Tetrahedron Lett.*, 2009, **50**, 6968; (*l*) K. C. Majumdar, B. Chattopadhyay and S. Samanta, *Tetrahedron Lett.*, 2009, **50**, 3178.
2 (*a*) I. A. McDonald, J. M. Lacoste, P. Bey, M. G. Palfreyman and M. Zreika, *J. Med. Chem.*, 1985, **28**, 186; (*b*) T. M. Bargar, R. J. Broersma, L. C. Creemre, J. R. McCarthy, J.-M. Hornsperger, M. G. Palfreyman, J. Wagner and M. J. Jung, *J. Med. Chem.*, 1986, **29**, 315; (*c*) R. O. Hutchins, J. Wei and S. J. Rao, *J. Org. Chem.*, 1994, **59**, 4007; (*d*) E.

Fuglseth, E. Otterholt, H. Høgmoen, E. Sundby, C. Charnock and B. H. Hoff, *Tetrahedron*, 2009, **65**, 9807.
3 For reviews, see: (*a*) R. B. Cheik, R. Chaabouni Laurent, P. Mison and A. Nafti, *Synthesis*, 1983, 685; (*b*) M. Johannsen and K. A. Jørgensen, *Chem. Rev.*, 1998, **98**, 1689; See also: (*c*) C. B. Jacobsen, L. Lykke, D. Monge, M. Nielsen, L. K. Ransborg and K. A. Jorgensen, *Chem. Commun.*, 2009, 6554.
4 For selected references, see: (*a*) B. M. Trost and E. Keinan, *J. Org. Chem.*, 1979, **44**, 3451; (*b*) Y. Inoue, M. Taguchi, M. Toyofuku and H. Hashimoto, *Bull. Chem. Soc. Jpn.*, 1984, **57**, 3021; (*c*) S. Bistrom, R. Aslanian and J. E. Bäckvall, *Tetrahedron Lett.*, 1985, **26**, 1749; (*d*) R. D. Connell, T. Rein, B. Akermark and P. Helquist, *J. Org. Chem.*, 1988, **53**, 3845; (*e*) S.-I. Murahashi, Y. Taniguchi, I. Yasushi and Y. Tanigawa, *J. Org. Chem.*, 1989, **54**, 3292; (*f*) M. Kawatsura, T. Hirakawa, T. Tanaka, D. Ikeda, S. Hayase and T. Itoh, *Tetrahedron Lett.*, 2008, **49**, 2450; (*g*) T. Nemoto, S. Tamura, T. Sakamoto and Y. Hamada, *Tetrahedron: Asymmetry*, 2008, **19**, 1751; (*h*) T. Nagano and S. Kobayashi, *J. Am. Chem. Soc.*, 2009, **131**, 4200.
5 (*a*) Y. Yokoyama, N. Takagi, H. Hikawa, S. Kaneko, N. Tsubaki and H. Okuno, *Adv. Synth. Catal.*, 2007, **349**, 662; (*b*) T. Nishikata and B. H. Lipshutz, *Org. Lett.*, 2009, **11**, 2377.
6 (*a*) S. A. Reed and M. C. White, *J. Am. Chem. Soc.*, 2008, **130**, 3316; (*b*) G. Liu, G. Yin and L. Wu, *Angew. Chem., Int. Ed.*, 2008, **47**, 4733; (*c*) S. A. Reed, A. R. Mazzotti and M. C. White, *J. Am. Chem. Soc.*, 2009, **131**, 11701.
7 (*a*) D. F. Fischer, Z.-q. Xin and R. Peters, *Angew. Chem., Int. Ed.*, 2007, **46**, 7704; (*b*) S. Jautze, P. Seiler and R. Peters, *Chem.–Eur. J.*, 2008, **14**, 1430.
8 For selected references, see: (*a*) N. J. Malek and A. E. Moormann, *J. Org. Chem.*, 1982, **47**, 5395; (*b*) A. Arcadi, E. Bernocchi, S. Cacchi, L. Caglioti and F. Marinelli, *Tetrahedron Lett.*, 1990, **31**, 2463; (*c*) J. Wu, J.-F. Marcoux, I. W. Davies and P. J. Reider, *Tetrahedron Lett.*, 2001, **42**, 159; (*d*) S. Merten, R. Froehlich, O. Kataeva and P. Metz, *Adv. Synth. Catal.*, 2005, **347**, 754; (*e*) X. Beebe, V. Gracias and S. W. Djuric, *Tetrahedron Lett.*, 2006, **47**, 3225; (*f*) E. M. Beccalli, G. Broggini, M. Martinelli, N. Masciocchi and S. Sottocornola, *Org. Lett.*, 2006, **8**, 4521; (*g*) L. El Kaim, M. Gizzi and L. Grimaud, *Org. Lett.*, 2008, **10**, 3417; (*h*) S. G. Stewart, C. H. Heath and E. L. Ghisalberti, *Eur. J. Org. Chem.*, 2009, 1934.
9 For recent selected references, see: (*a*) K. P. da Silva, M. N. Godoi and C. R. D. Correia, *Org. Lett.*, 2007, **9**, 2815; (*b*) A. V. Moro, F. S. P. Cardoso and C. R. D. Correia, *Tetrahedron Lett.*, 2008, **49**, 5668; (*c*) F.-X. Felpin, E. Fouquet and C. Zakri, *Adv. Synth. Catal.*, 2008, **350**, 2559; (*d*) F.-X. Felpin, O. Ibarguren, L. Nassar-Hardy and E. Fouquet, *J. Org. Chem.*, 2009, **74**, 1349; (*e*) A. H. L. Machado, M. A. de Sousa, D. C. S. Patto, L. F. S. Azevedo, F. I. Bombonato and C. R. D. Correia, *Tetrahedron Lett.*, 2009, **50**, 1222; (*f*) B. Ahmed-Omer, D. A. Barrow and T. Wirth, *Tetrahedron Lett.*, 2009, **50**, 3352; (*g*) F.-X. Felpin, J. Coste, C. Zakri and E. Fouquet, *Chem.–Eur. J.*, 2009, **15**, 7238; (*h*) A. V. Moro, F. S. P. Cardoso and C. R. D. Correia, *Org. Lett.*, 2009, **11**, 3642; (*i*) B. Schmidt and F. Hoelter, *Chem.–Eur. J.*, 2009, **15**, 11948; (*j*) S. Cacchi, G. Fabrizi, A. Goggiamani and A. Sferrazza, *Synlett*, 2009, 973; (*k*) S. Cacchi, G. Fabrizi, A. Goggiamani and A. Sferrazza, *Synlett*, 2009, 1277; (*l*) J. C. Pastre and C. R. D. Correia, *Adv. Synth. Catal.*, 2009, **351**, 1217; (*m*) A. V. Moro, F. S. P. Cardoso and C. R. D. Correia, *Org. Lett.*, 2009, **11**, 3642; (*n*) A. H. L. Machado, M. A. de Sousa, D. C. S. Patto, L. F. S. Azevedo, F. I. Bombonato and C. R. D. Correia, *Tetrahedron Lett.*, 2009, **50**, 1222; (*o*) F. A. Siqueira, J. G. Taylor and C. R. D. Correia, *Tetrahedron Lett.*, 2010, **51**, 2102; For a review on the palladium chemistry of arenediazonium salts, see: (*p*) A. Roglans, A. Pla-Quintana and M. Moreno-Mañas, *Chem. Rev.*, 2006, **106**, 4622.
10 For a comprehensive overview of the Heck reaction, see: *The Mizoroki–Heck Reaction*, Ed M. Oestreich, John Wiley & Sons, Ltd, Chichester, UK10.1002/9780470716076.ch1.
11 (*a*) S. Cacchi, G. Fabrizi, A. Goggiamani and D. Persiani, *Org. Lett.*, 2008, **10**, 1597; (*b*) G. Bartoli, S. Cacchi, G. Fabrizi and A. Goggiamani, *Synlett*, 2008, 2508; (*c*) G. Fabrizi, A. Goggiamani, A. Sferrazza and S. Cacchi, *Angew. Chem. Int. Ed.*, 2010, **49**, 4067; (*d*) S. Cacchi, G. Fabrizi, A. Goggiamani, A. Perboni, A. Sferrazza and P. Stabile, *Org. Lett.*, 2010, **12**, 3279; (*e*) R. Berrino, S. Cacchi, G. Fabrizi, A. Goggiamani and P. Stabile, *Org. Biomol. Chem.*, 2010, **8**, 4518.
12 For recent reviews on the palladium chemistry of indoles, see: (*a*) F. Alonso, I. P. Beletskaya and M. Yus, *Chem. Rev.*, 2004, **104**, 3079; (*b*) G. Zeni and R. C. Larock, *Chem. Rev.*, 2004, **104**, 2285; (*c*) S. Cacchi and G. Fabrizi, *Chem. Rev.*, 2005, **105**, 2873; (*d*) G. R. Humphrey and J. T. Kuethe, *Chem. Rev.*, 2006, **106**, 2875; (*e*) S. Patil and J. K. Buolamwini, *Curr. Org. Synth.*, 2006, **3**, 477; (*f*) L. Ackermann, *Synlett*, 2007, 507; (*g*) D. Alberico, M. E. Scott and M. Lautens, *Chem. Rev.*, 2007, **107**, 174; (*h*) K. Krüger (née Alex), A. Tillack and M. Beller, *Adv. Synth. Catal.*, 2008, **350**, 2153; (*i*) L. Joucla and L. Djakovitch, *Adv. Synth. Catal.*, 2009, **351**, 673.
13 For a review, see: (*a*) G. Battistuzzi, S. Cacchi and G. Fabrizi, *Eur. J. Org. Chem.*, 2002, 2671; (*b*) See also: S. Cacchi, G. Fabrizi and P. Pace, *J. Org. Chem.*, 1998, **63**, 1001.
14 H. Brunner, N. Le Courtirier de Courcy and J.-P. Genêt, *Tetrahedron Lett.*, 1999, **40**, 4815.

