Tetrahedron Letters 52 (2011) 3329–3332

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Palladium-catalyzed stereoselective synthesis of 3-(aminomethylene)-oxindoles

Morteza Bararjanian [a], Saeedeh Hosseinzadeh [a], Saeed Balalaie [a,*], Hamid Reza Bijanzadeh [b], Eckardt Wolf [c]

[a] Peptide Chemistry Research Center, K.N. Toosi University of Technology, PO Box 15875-4416, Tehran, Iran
[b] Department of Chemistry, Tarbiat Modares University, PO Box 141115-175, Tehran, Iran
[c] Tofigh Daru Res. & Eng. Co., 61st St. km 18 Karaj Highway, Tehran 37515-375, Iran

ARTICLE INFO

Article history:
Received 14 February 2011
Revised 4 April 2011
Accepted 18 April 2011
Available online 24 April 2011

Dedicated to Professor Ali Seyyedi Isfahani on the occasion of his 75th birthday.

Keywords:
Carbopalladative cyclization
Buchwald reaction
3-(Aminoarylmethylene)-oxindoles
Active acetylenic compounds
Stereoselective synthesis

ABSTRACT

An efficient palladium-catalyzed protocol for the stereoselective synthesis of 3-(aminoarylmethylene)-oxindoles has been developed. In this approach, Ugi-4-component reaction adducts were used as starting materials for carbopalladative cyclization–Buchwald reaction sequences.

The design of new sequencing MCRs (multi-component reactions) with subsequent transformations, including, for example, cyclization, and formation of new functional groups is a very useful procedure for developing molecular architectures.[1] Meanwhile, the sequencing of MCRs is a promising synthetic strategy for generating collections of molecules by DOS (Diversity Oriented Synthesis). This is an emerging field involving the synthesis of combinatorial libraries of diverse small molecules for biological screening.[2]

Oxindoles are an important class of heterocycles which are often found in bioactive molecules as the key substructure.[3] Substituted 3-methylene-oxindoles which contain a heteroatom in the exocyclic alkene also play important roles within the class of functionalized oxindoles, for example, (*Z*)-3-(aminomethylene)-oxindoles have been identified as protein kinase inhibitors,[4] and include examples such as BIBF 1120,[5] GW8510,[6] and GW491619,[7] and the recently identified Aurora B inhibitor, hesperadin[8] (Fig. 1).

Furthermore, 3-(aminomethylene)-oxindoles are versatile precursors for further synthetic manipulations and have been employed widely in total syntheses of natural products, and for the preparation of novel nonnatural compounds.[9] There are several approaches for the synthesis of 3-(aminomethylene)-oxindoles, including: (a) syn-aminopalladation of α,β-acetylenic amides using phthalimide in the presence of palladium acetate and $PhI(OAc)_2$;[10] (b) cyclization of 2-alkynyl aryl isocyanates with amides, carbamates or sulfonamides;[11] (c) reaction of 3-chloroalkylidene-oxindoles with amines;[12] (d) sequential carbonylation of 2-alkynylanilines in the presence of $CuCl_2$;[13] (e) cyclization of 2-alkynyl isocyanates in the presence of $FeCl_3$ followed by nucleophilic addition under microwave irradiation.[14]

Although a number of methods are available for the synthesis of these oxindoles, the reported methods have some drawbacks, including lack of generality, limited functional group tolerance, lengthy synthetic sequences, and harsh reaction conditions. The need for the development of a stereoselective and diversity oriented approach for the synthesis of these compounds is of interest and a considerable challenge for organic chemists. Our previous research to develop novel reactions[15] combined with the biological activities of various 3-(aminoarylmethylene)-oxindoles has prompted us to develop sequential reactions to access these heterocycles.

A retrosynthetic analysis suggested the formation of an exocyclic double bond in 3-(aminoarylmethylene)-oxindoles via ring-closure of N-substituted 2-alkynylamides **I** (resulting from the Ugi-4-component reaction of an aldehyde **1**, a 2-haloaniline **2**, a propiolic acid **3**, and an isocyanide **4**), through a carbopalladative cyclization–Buchwald reaction[16] using a Pd-catalyst (Scheme 1).

On the basis of our recent developments on post-functionalization of multi-component reaction (MCR) sequences, we designed a procedure for the efficient conversion of Ugi-4MCR intermediates **I** into 3-(aminoarylmethylene)-oxindoles as shown in Scheme 2. Palladium/phosphine-catalyzed cyclization of N-substituted-2-alkynylamides **I** with secondary amines produces the 3-(aminoarylmethylene)-

* Corresponding author.
E-mail address: Balalaie@kntu.ac.ir (S. Balalaie).

0040-4039/$ - see front matter © 2011 Published by Elsevier Ltd.
doi:10.1016/j.tetlet.2011.04.071

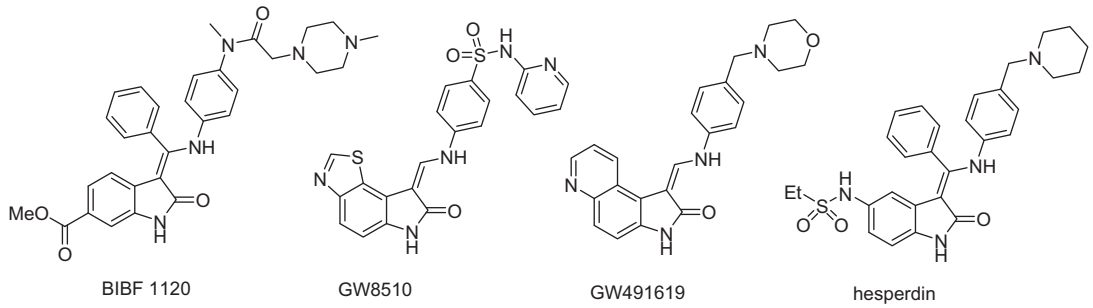


Figure 1. Oxindole-based kinase inhibitors.

oxindoles via sequential carbopalladative cyclization–Buchwald reactions.

The Ugi reaction has several advantages such as wide scope, high variability (four diversity points), generates multifunctional adducts, and allows the possibility to carry out subsequent transformations. Several post-transformations on Ugi products have been reported, such as cyclocondensation,[17] radical cyclization,[18] S_NAr,[19] S_N2,[20] and S_N2' reactions[21] and metathesis reactions.[22]

In all cases various cyclic scaffolds were obtained. The combination of rich and diverse palladium-catalyzed chemistry with the Ugi reaction has also been investigated.[23] A number of medicinally active heterocycles were synthesized using the Heck reaction, N-arylation, C-arylation of a benzylic carbon, C–H functionalization, the Suzuki–Miyaura reaction and Sonogashira coupling, on properly functionalized Ugi adducts.[24] In most cases, the efficiency of these reactions depends on the type of functionality in the Ugi-products. In the present approach, N-substituted 2-alkynylamides I were synthesized via the four-component reaction of benzaldehydes 1, 2-iodoaniline (**2**), phenyl propiolic acid (**3**) and isocyanides **4**.[15a] The reaction of secondary amines with N-substituted-2-alkynylamides I catalyzed by $Pd(OAc)_2$ in the presence of Cs_2CO_3 led to the formation of 3-(aminoarylmethylene)-oxindoles. The results are summarized in Table 1.

Optimization of the reaction conditions was carried out for the synthesis of compound **6a** as a model substrate. The Ugi-4MCR product **Ia** from the reaction of benzaldehyde (**1a**), 2-iodoaniline (**2**), phenylpropiolic acid (**3**) and cyclohexylisocyanide (**4a**) in MeOH, was chosen to screen the domino carbopalladative cyclization–Buchwald coupling reaction. $Pd(OAc)_2$ as the catalyst precursor, several bases and phosphine ligands were examined to establish standard reaction conditions for the addition of morpholine. K_2CO_3, Cs_2CO_3 and Et_3N were used under identical conditions and the best results were obtained using Cs_2CO_3. Whereas PPh_3 as the ligand led to low yields, the reaction with tri(2-furyl)phosphine and racemic-BINAP gave the desired product in good yield. Tri(2-furyl)phosphine was chosen as the preferred ligand due to it being more cost-effective.

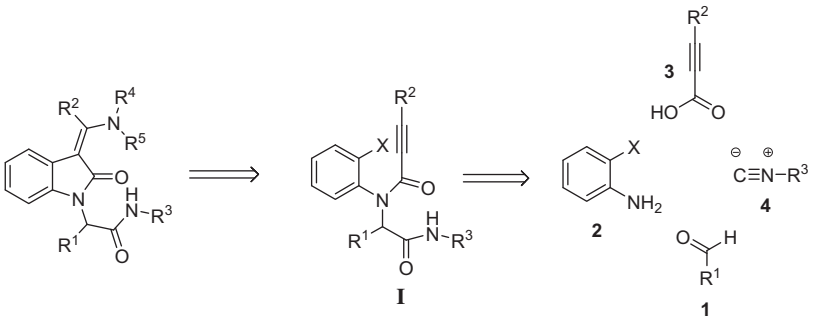
We were pleased to find that under the optimized conditions reaction of *N*-[(cyclohexylcarbamoyl) (phenyl)methyl]-*N*-(2-iodophenyl)-3-phenylpropionamide (**Ia**) (1 mmol), morpholine (**5a**) (2 mmol, 2 equiv), tri(2-furyl)phosphine (0.1 mmol, 0.1 equiv), $Pd(OAc)_2$ (0.05 mmol, 0.05 equiv), and Cs_2CO_3 (2 mmol, 2 equiv) in toluene (20 mL) under reflux for 12 h, yielded 80% of the desired product (**6a**) (Table 1). Gratifyingly, we found that this transformation was general for compound I derived from a wide range of benzaldehydes, isocyanides, and secondary amines providing an easy access to highly substituted 3-(aminoarylmethylene)-2-oxindoles **6a**-**k** with Z-configuration (Table 1).

The Z-configuration of the products was confirmed using ^1H NMR spectroscopy with a diagnostic signal for the Z-isomer observed at δ 5.56–5.64 (H-4 of the oxindole). This unusual high-field shift is related to the aromatic ring current of the phenyl ring. For an indication of the stereoselectivity of this reaction, the chemical shifts of the H-4 proton were compared with those of the reported analogues.[14] NOE experiments on compound **6g** further confirmed the structure as the Z-isomer.

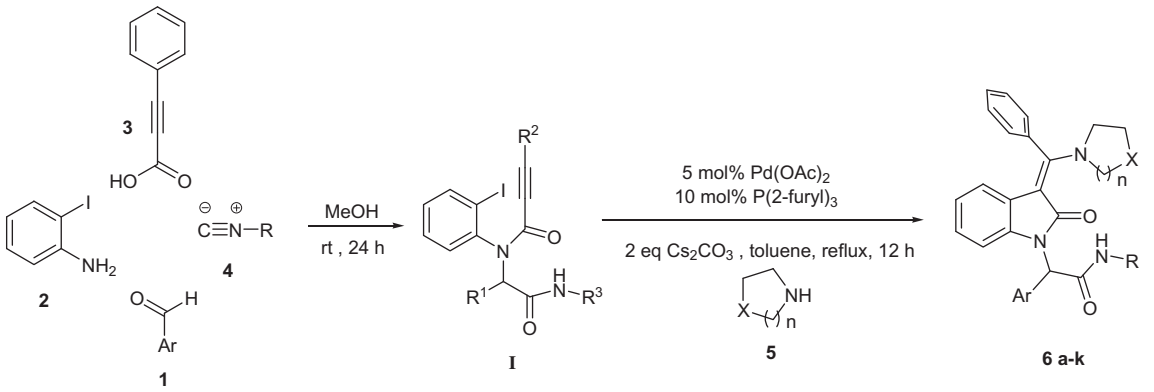
According to known palladium chemistry, the domino carbopalladative cyclization–Buchwald reaction can be categorized as follows: (1) oxidative addition of haloarene **I** to Pd(0); (2) insertion of palladium on the alkyne moiety (carbopalladation); (3) nucleophilic addition of the secondary amine; (4) reductive elimination to afford the 3-(aminoarylmethylene)-oxindoles **6a–k** with regeneration of the Pd(0) species.

In conclusion, an efficient approach for the stereoselective synthesis of (*Z*)-3-(aminoarylmethylene)-oxindoles has been developed via palladium-catalyzed Ugi-carbopalladative cyclization–Buchwald reaction sequences. Overall these reactions accomplish both intramolecular C–C bond formation and intermolecular C–N bond formation across a carbon–carbon triple bond in a regioselective fashion. High bond forming efficiency (BFE), good yields, and stereoselective syntheses of 3-(aminoarylmethylene)-oxindoles via diversity oriented synthesis (DOS) have been established.

General procedure for the synthesis of 3-(aminoarylmethylene)-oxindoles **6a**–**k**: 2-Iodoaniline (**2**) (219 mg, 1 mmol), benzaldehyde **1** (1 mmol), and MeOH (5 mL) were stirred for 30 min. Then, phenyl propiolic acid (**3**) (146 mg, 1 mmol) and, after 15 min, isocyanide **4** (1 mmol) were added, and the mixture stirred at ambient temperature for 24 h. The progress of the reaction was

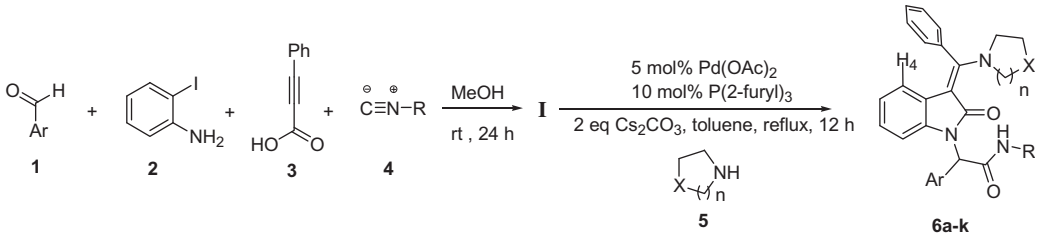


Scheme 1. Retrosynthetic pathway for the synthesis of 3-(aminoarylmethylene)-oxindoles.



Scheme 2. Stereoselective synthesis of (*Z*)-3-(aminoarylmethylene)-oxindoles through sequential reactions.

Table 1
Synthesis of (*Z*)-3-(aminoarylmethylene)-oxindoles via Ugi-carbopalladative cyclization–Buchwald reaction sequences



Product	Ar	R	X	*n*	Yield[a] (%)
6a	C_6H_5	Cy[b]	O	2	80
6b	C_6H_5	Cy	CH_2	2	78
6c	C_6H_5	*t*-Bu	N–CH_2CH_2OH	2	70
6d	C_6H_5	*t*-Bu	N–Me	2	85
6e	C_6H_5	*t*-Bu	O	2	83
6f	C_6H_5	*t*-Bu	CH_2	2	80
6g	C_6H_5	*t*-Bu	CH_2	1	76
6h	4-NC–C_6H_4	Bn	O	2	63
6i	4-Me_2N–C_6H_4	Cy	O	2	84
6j	4-MeC_6H_4	Cy	O	2	77
6k	4-$MeOC_6H_4$	Cy	O	2	82

[a] Isolated yield.
[b] Cy = cyclohexyl.

monitored by TLC (eluent: hexane/EtOAc, 5:1). Upon completion, the mixture was diluted with saturated $NaHCO_3$ solution (30 mL) and extracted with EtOAc (3×20 mL). The combined organic phase was dried over Na_2SO_4 and the solvent removed under reduced pressure. The crude Ugi adduct was added to a flask containing toluene (20 mL), $Pd(OAc)_2$ (11 mg, 0.05 equiv), Cs_2CO_3 (652 mg, 2 mmol), tri(2-furyl)phosphine (23 mg, 0.1 equiv) and the secondary amine (2 mmol). The resulting mixture was heated at reflux for 12 h. After cooling, the mixture was washed with brine (2×30 mL) and the organic phase collected. The organic layer was dried over Na_2SO_4, filtered and concentrated in vacuo. Purification by column chromatography on silica gel (hexane/EtOAc) gave products **6a–k** in 63–85% yield.

N-Cyclohexyl-2-{(*Z*)-3-[morpholino(phenyl)methylene]-oxindolin-1-yl}-2-phenylacetamide (**6a**) 0.416 g, 80%; mp: 206 °C (decomposed); IR (KBr, cm^{-1}): 3277, 2934, 1687, 1637, 1555; ^1H NMR (500 MHz, $CDCl_3$): δ 1.12–1.93 (m, 10H, $H_{cyclohexyl}$), 3.60 (br s, 4H, CH_2O), 3.86–3.90 (m, 5H, CH_2N and $H_{cyclohexyl}$), 5.63 (d, 1H, J = 7.8 Hz, H_{Ar}), 6.31 (s, 1H, CH), 6.53 (m, 1H, H_{Ar}), 6.64 (d, 1H, J = 6.5 Hz, NH), 6.81 (m, 2H, H_{Ar}), 7.25–7.55 (m, 10H, H_{Ar}); ^{13}C NMR (125 MHz, $CDCl_3$): δ 24.5, 24.6, 25.5, 32.7, 32.8, 48.4, 52.8, 59.2, 67.6, 97.9, 109.8, 119.0, 120.5, 122.7, 126.6, 127.6, 127.8, 128.4, 129.5, 129.6, 130.3, 130.6, 131.2, 135.2, 135.6, 137.0, 161.6, 165.0, 167.8; mass: HR-MS (ESI) calcd for $C_{33}H_{36}N_3O_3$ $[M+1]^+$ 522.27516, found 522.27512.

*N*Cyclohexyl-2-{(*Z*)-2-oxo-3-[phenyl(piperidin-1-yl)methylene] oxindolin-1-yl}-2-phenylacetamide (**6b**) 0.405 g, 78%; mp: 273 °C (decomposed); IR (KBr, cm^{-1}): 3263, 2930, 1683, 1635, 1560; ^1H NMR (500 MHz, $CDCl_3$): δ 1.12–2.00 (m, 16H, $H_{cyclohexyl}$ and $H_{Piperidyl}$), 3.45–3.64 (m, 4H, $2CH_2$, CH_2N), 3.86–3.92 (m, 1H, $H_{cyclohexyl}$), 5.63 (d, 1H, J = 7.7 Hz, H4, H_{Ar}), 6.33 (s, 1H, CH), 6.53 (t, 1H, J = 7.5 Hz, H_{Ar}), 6.78 (d, 1H, J = 7.5 Hz, H_{Ar}), 6.82 (t, 1H, J = 7.7 Hz, H_{Ar}), 6.88 (br s, 1H, NH), 7.23–7.60 (m, 10H, H_{Ar}); ^{13}C NMR (125 MHz, $CDCl_3$): δ 23.8, 24.5, 24.6, 25.6, 27.4, 32.7, 48.3, 53.1, 59.3, 97.1, 109.5, 118.7, 120.4, 122.1, 127.0, 127.4, 127.7, 128.3, 129.2, 129.3, 130.2, 130.5, 131.0, 135.9, 136.0, 136.6, 162.8,

165.0, 168.1; mass: HR-MS (ESI) calcd for $C_{34}H_{38}N_3O_2$ $[M+1]^+$ 520.29589, found 520.29585.

Acknowledgments

S.B. and M.B. gratefully acknowledge the Alexander von Humboldt foundation for research fellowships. We are grateful to Professor R. Gleiter for helpful discussions. We express our gratitude to Mr. M. Jalilevand, managing director of Kimia Exir Company for donation of chemicals and financial support.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2011.04.071.

References and notes

1. (a) Dömling, A. In *Multicomponent Reactions*; Zhu, J., Bienaymé, H., Eds.; Wiley-VCH: Weinheim, 2005; pp 76–95; (b) Tietze, L. F. *Chem. Rev.* **1996**, *96*, 115–136; (c) Tietze, L. F.; Brasche, G.; Gericke, K. M. *Domino Reactions in Organic Synthesis*; Wiley-VCH: Weinheim, 2006. pp 542-565; (d) Tietze, L. F. In *Stimulating Concepts in Chemistry*; Shibasaki, M., Stoddart, J. F., Eds.; Wiley-VCH: Weinheim, 2000; pp 39–64; (e) Dömling, A.; Ugi, I. *Angew. Chem., Int. Ed.* **2000**, *39*, 3168; (g) Dömling, A. *Chem. Rev.* **2006**, *106*, 17–89.
2. (a) Isambert, N.; Lavilla, R. *Chem. Eur. J.* **2008**, *14*, 8444–8454; (b) Arndtsen, B. A. *Chem. Eur. J.* **2009**, *15*, 302–313; (c) Sunderhaus, J. D.; Martin, S. F. *Chem. Eur. J.* **2009**, *15*, 1300–1308.
3. (a) Marti, C.; Carreira, E. M. *Eur. J. Org. Chem.* **2003**, 2209–2218; (b) Galliford, C. V.; Scheidt, K. A. *Angew. Chem., Int. Ed.* **2007**, *46*, 8748–8758.
4. (a) Treu, M.; Guertler, U.; Karner, T.; Kraemer, O.; Quant, J. J.; Zahn, S. K. WO 200815 2013 A1, *Chem. Abstr.* **2009**, *150*, 55987y.; (b) Treu, M.; Mantoulidis, A.; Tontsch-Grunt, U. WO2007122219 A1, *Chem. Abstr.* **2007**, *147*, 502230v.; (c) Heckel, A.; Roth, G. R.; Joerg, K.; Hoerer, S.; Uphues, I. US20050203104 A1, *Chem. Abstr.* **2005**, *143*, 306172f.; (d) Burgdorf, L. T.; Bruge, D.; Greiner, H.; Kordowicz, M.; Sirrenberg, C.; Zenke, F. (Merck Patent) WO2006131186 A1, *Chem. Abstr.* **2006**, *146*, 62590j.
5. (a) Hilberg, F.; Roth, G. J.; Krssak, M.; Kautschitsch, S.; Sommergruber, W.; Grunt, U. T.; Chesa, P. G.; Bader, G.; Zoephel, A.; Quant, J.; Heckel, A.; Rettig, W. R. *Cancer Res.* **2008**, *68*, 4774–4782; (b) Roth, G. J.; Heckel, A.; Colbatzky, F.; Handschuh, S.; Kley, J.; Lehmann-Lintz, T.; Lotz, R.; Tontsch-Grunt, U.; Walter, R.; Hilberg, F. *J. Med. Chem.* **2009**, *52*, 4466–4480.
6. Johnson, K.; Liu, L.; Majdzadeh, N.; Chavez, C.; Chin, P. C.; Morrison, B.; Wang, L.; Park, J.; Chugh, P.; Chen, H. -M.; D'Mello, S. R. *J. Neurochem.* **2005**, *93*, 538.
7. Eberwein, D. J.; Harrington, L.; Griffin, R.; Tadepalli, S.; Knick, V.; Phillips, K.; Dickerson, S.; Davies, S. *Proc. Am. Assoc. Cancer Res.* **2002**, *43*. abstract 1611.
8. Hauf, S.; Cole, R. W.; LaTerra, S.; Zimmer, C.; Schnapp, G.; Walter, R.; Heckel, A.; van Meel, J.; Rieder, C. L.; Peters, J. M. *J. Cell Biol.* **2003**, *161*, 281.
9. Trost, B. M.; Brennan, M. K. *Synthesis* **2009**, 3003–3025.
10. Tang, S.; Peng, P.; Pi, S. F.; Liang, Y.; Wang, N.-X.; Li, J. H. *Org. Lett.* **2008**, *10*, 1179–1182.
11. Miura, T.; Toyoshima, T.; Takahashi, Y.; Murakami, M. *Org. Lett.* **2009**, *11*, 2141–2143.
12. (a) Beccalli, E. M.; Marchesini, A.; Pilati, T. *Tetrahedron* **1994**, *50*, 12697–12712; (b) Beccalli, E. M.; Marchesini, A. *Tetrahedron* **1995**, *51*, 2353–2362.
13. Tang, S.; Yu, Q. F.; Peng, P.; Li, J. H.; Zhong, P.; Tang, R. Y. *Org. Lett.* **2007**, *9*, 3413–3416.
14. Cantagrel, G.; de Carné-Carnavalet, B.; Meyer, C.; Cossy, J. *Org. Lett.* **2009**, *11*, 4262–4265.
15. (a) Bararjanian, M.; Balalaie, S.; Rominger, F.; Movassagh, B.; Bijanzadeh, H. R. *J. Org. Chem.* **2010**, *75*, 2806–2812; (b) Bararjanian, M.; Balalaie, S.; Movassagh, B.; Bijanzadeh, H. R. *Tetrahedron Lett.* **2010**, *51*, 3277–3279.
16. (a) D'Souza, D. M.; Müller, T. J. J. *Chem. Soc. Rev.* **2007**, *36*, 1095–1108; (b) D'Souza, D. M.; Muschelknautz, C.; Rominger, F.; Müller, T. J. J. *Org. Lett.* **2010**, *12*, 3364–3367; (c) Schönhaber, J.; Frank, W.; Müller, T. J. J. *Org. Lett.* **2010**, *12*, 4122–4125.
17. (a) Nixey, T.; Tempest, P.; Hulme, C. *Tetrahedron Lett.* **2002**, *43*, 1637–1639; (b) Marcaccini, S.; Pepino, R.; Pozo, M. C.; Basurto, S.; Garcia-Valverde, M.; Torroba, T. *Tetrahedron Lett.* **2004**, *45*, 3999–4001; (c) Corres, N.; Delgado, J. J.; Garcia-Valverde, M.; Marcaccini, S.; Rodriguez, T.; Rojo, J.; Torroba, T. *Tetrahedron* **2008**, *64*, 2225–2232.
18. (a) El Kaim, L.; Grimaud, L.; Miranda, L. D.; Vieu, E. *Tetrahedron Lett.* **2006**, *47*, 8259–8261; (b) El Kaim, L.; Grimaud, L.; Vieu, E. *Org. Lett.* **2007**, *9*, 4171–4173.
19. (a) Cristau, P.; Vors, J. P.; Zhu, J. *Org. Lett.* **2001**, *3*, 4079–4082; (b) Tempest, P.; Ma, V.; Kelly, M. G.; Jones, W.; Hulme, C. *Tetrahedron Lett.* **2001**, *42*, 4963–4968; (c) Cristau, P.; Vors, J. P.; Zhu, J. *Tetrahedron* **2003**, *59*, 7859–7870; (d) Spatz, J. H.; Umkehrer, M.; Kalinski, C.; Ross, G.; Burdack, C.; Kolb, J.; Bach, T. *Tetrahedron Lett.* **2007**, *48*, 8060–8064.
20. (a) Ugi, I.; Schmid, T. *J. Prakt. Chem.* **1997**, *339*, 652–655; (b) Umkehrer, M.; Kolb, J.; Burdack, C.; Ross, G.; Hiller, W. *Tetrahedron Lett.* **2004**, *45*, 6421–6424; (c) Neo, A. G.; Delgado, J.; Marcaccini, C. S.; Marcos, C. F. *Tetrahedron Lett.* **2005**, *46*, 23–26; (d) Golebiowski, A.; Klopfenstein, S. R.; Shao, X.; Chen, J. J.; Colson, A. O.; Grieb, A. L.; Russell, A. F. *Org. Lett.* **2000**, *2*, 2615–2617; (e) de Greef, M.; Abeln, S.; Belkasmi, K.; Dömling, A.; Orru, R. V. A.; Wessjohann, L. A. *Synthesis* **2006**, 3997–4004; (f) Xing, X.; Wu, J.; Feng, G.; Dai, W. M. *Tetrahedron* **2006**, *62*, 6774–6781; (g) Banfi, L.; Riva, R.; Basso, A. *Synlett* **2010**, 23–41.
21. Banfi, L.; Basso, A.; Cerulli, V.; Guanti, G.; Riva, R. *J. Org. Chem.* **2008**, *73*, 1608–1611.
22. Dietrich, S. A.; Banfi, L.; Basso, A.; Damonte, G.; Guanti, G.; Riva, R. *Org. Biomol. Chem.* **2005**, *3*, 97–106.
23. (a) Tsuji, J. *Palladium Reagents and Catalysts*; Wiley-VCH: Chichester, 2004; (b)*Metal-Catalyzed Cross-Coupling Reactions*; de Meijere, A., Diederich, F., Eds.; Wiley-VCH: Weinheim, 2004.
24. (a) Erb, W.; Neuville, L.; Zhu, J. *J. Org. Chem.* **2009**, *74*, 3109–3115. and references cited therein; (b) Bonnaterre, F.; Bois-Choussy, M.; Zhu, J. *Org. Lett.* **2006**, *8*, 4351–4354; (c) Salcedo, A.; Neuville, L.; Zhu, J. *J. Org. Chem.* **2008**, *73*, 3600–3603; (d) Bonnaterre, F.; Bois-Choussy, M.; Zhu, J. *Beilstein J. Org. Chem.* **2008**, 1–11; (e) Kalinski, C.; Umkehrer, M.; Ross, G.; Kolb, J.; Burdack, C.; Hillerb, W. *Tetrahedron Lett.* **2006**, *47*, 3423–3426; (f) Kalinski, C.; Umkehrer, M.; Schmidt, J.; Ross, G.; Kolb, J.; Burdack, C.; Hillerb, W.; Hoffmann, S. D. *Tetrahedron Lett.* **2006**, *47*, 4683–4686.