RSC Advances

PAPER

View Article Online
View Journal | View Issue

Cite this: *RSC Adv.*, 2016, **6**, 75202

Iodine-mediated regioselective guanylation-amination of propargylamines towards the synthesis of diversely substituted 2-aminoimidazoles†

Pavel Fedoseev, Nandini Sharma, Rupesh Khunt, Denis S. Ermolat'ev and Erik V. Van der Eycken*

Received 23rd May 2016
Accepted 3rd August 2016

DOI: 10.1039/c6ra13371a

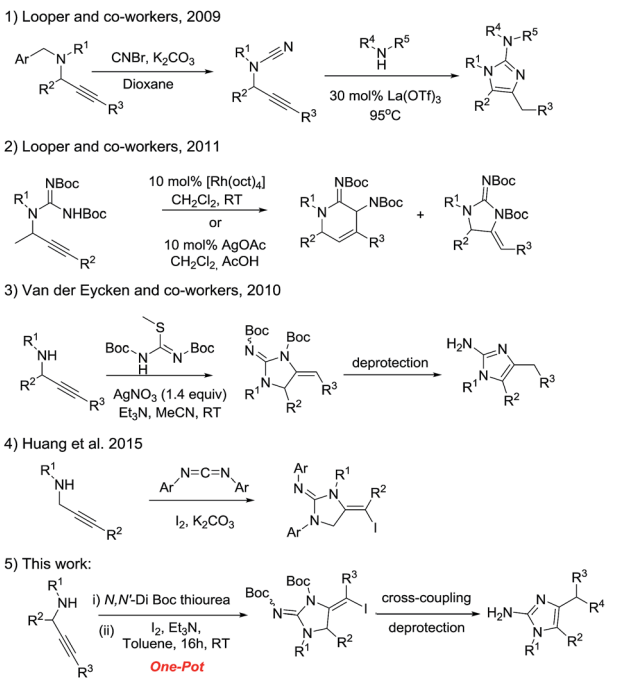
www.rsc.org/advances

A diversity-oriented approach for the synthesis of 2-aminoimidazoles is presented. The method involves the cyclization of secondary propargylamines using iodine allowing the generation of diversely-substituted 2-aminoimidazoles. The iodo group generated during cyclization can be used for further modification, which is an additional asset of this method.

Introduction

Aromatic heterocyclic fragments are one of the most biologically relevant patterns found in many natural products and pharmaceuticals. Consequently considerable efforts are being done for the development of new methods for their construction. Among these, 2-aminoimidazoles are an important class of N-heterocycles, found extensively in biologically active marine natural sponge alkaloids.[1] Owing to their significant biological activity, they are often used as building blocks in pharmacologically active chemical entities. For instance, polysubstituted 2-aminoimidazoles have been reported as inhibitors of the binuclear manganese metalloenzyme human arginase I[2] and human β-secretase (BACE1),[3] as anti-cancer agents,[4] as sodium hydrogen exchanger-1 (NHE-1),[5] as α-adrenoreceptor agonists,[6] as antibiofilm agents,[7] as 5-HT_{2B} receptor antagonists[8] and for inhibition and breaking of advanced glycation end-products (AGEs).[9]

Though, a number of methods has been described to construct 2-aminoimidazoles,[10] the development of new routes allowing their facile synthesis from readily available starting materials would always be a welcome addition. In recent years, the preparation of 2-aminoimidazoles from propargylic compounds *via* metal-catalyzed heteroannulation, has represented one of the most attractive strategies in organic synthesis.[10e,11] The π-electrophilic character of the triple bond makes it a versatile entity for several chemical transformations. Moreover, propargylamines are easily prepared by the coupling of an amine, an aldehyde and an alkyne, known as the A^3-coupling reaction, which at the same time serves the purpose of the final scaffold diversification reaction.[12] In 2009, Looper and co-workers reported a La(III)-catalyzed guanidine–alkyne hydroamination–isomerization sequence for the rapid access to the 2-aminoimidazole core from propargylcyanamides (Scheme 1, entry 1). However, the process is limited by the availability of the starting electron-rich secondary benzylamines as well as by the



Scheme 1 Synthesis of substituted 2-aminoimidazoles from secondary propargylamines.

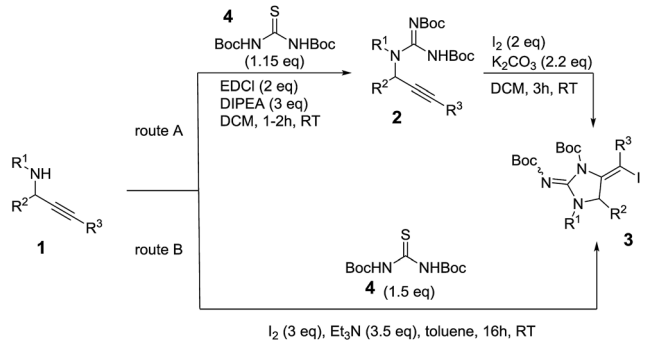
Laboratory for Organic & Microwave-Assisted Chemistry (LOMAC), Department of Chemistry, University of Leuven (KU Leuven), Celestijnenlaan 200F, B-3001 Leuven, Belgium. E-mail: erik.vandereycken@chem.kuleuven.be; Web: http://chem.kuleuven.be/en/research/mds/lomac

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c6ra13371a

harsh reaction conditions.[13] Later on, the same group developed another strategy to construct substituted 2-aminoimidazoles by a silver-mediated 5-*exo*-dig cyclization of di-Boc protected propargylguanidines (Scheme 1, entry 2).[14] However, the process suffered from poor selectivity as the 6-*endo*-dig product was observed in all cases. In 2010, our group reported a rapid and highly efficient silver(I)-mediated synthesis of 1,4,5-trisubstituted 2-aminoimidazoles from secondary propargylamines *via* a one-pot guanylation/cyclization strategy using protected S-methylisothiourea[10e] (Scheme 1, entry 3). The same methodology was extended to the synthesis of spiro-2-aminoimidazoles.[11b] In 2014, Wolfe and co-workers reported the synthesis of 2-aminoimidazoles *via* a Pd-catalyzed carboamination reactions of *N*-propargyl guanidines and aryl triflates with good product yields.[10g] However, the lack of diversity and the application of a multi-step synthesis of the starting material limited the facile preparation of natural product analogues containing this skeleton.

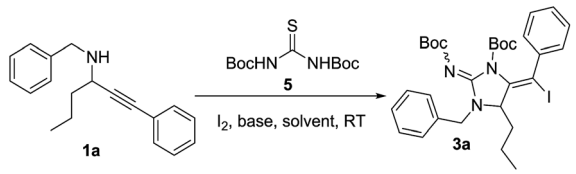
Although metal-catalyzed approaches are mostly selective and high yielding, they suffer from the inherent drawback of the presence of traces of metals in the final compounds, which might hamper or alter the biological activity. Owing to this, the development of metal-free approaches for the synthesis of such biologically important heterocycles is on the rise.[15] Recently, iodine-mediated metal-free cyclization approaches are gathering a lot of attention in synthetic chemistry. Iodine activates the alkyne very well, and most often, an iodo group will remain in the molecule after cyclization, allowing the introduction of additional functionalities.[16] Our interest in the biological activity of 2-aminoimidazoles and the development of diversity-oriented concise routes for the synthesis of biologically important heterocycles,[17] has prompted us to explore a new metal-free strategy for their synthesis. To the best of our knowledge, there is only one recently reported example of the formation of N-heterocycles based on iodocyclization[18] whereby imidazoline derivatives were synthesized by reaction between secondary propargylamines and aryl-substituted carbodiimides (Scheme 1, entry 4). However, the use of substituted carbodiimides for the *in situ* generation of the guanidine intermediate hampers the diversification of the generated products.

The proposed synthesis is based on three key steps: an A^3-coupling reaction to generate the secondary propargylamines, followed by their conversion to the corresponding guanidines using *N*,*N*′-bis-Boc-protected thiourea, and subsequent electrophilic iodocyclization to provide Boc-protected iminoimidazolidines. The generated polysubstituted compounds bear an iodo group, which can further participate in various cross-coupling reactions to enhance the diversity of the substituted pattern.



Scheme 2 Guanylation/iodocyclization of secondary propargylamines.

Table 1 Optimization of the reaction conditions[a]



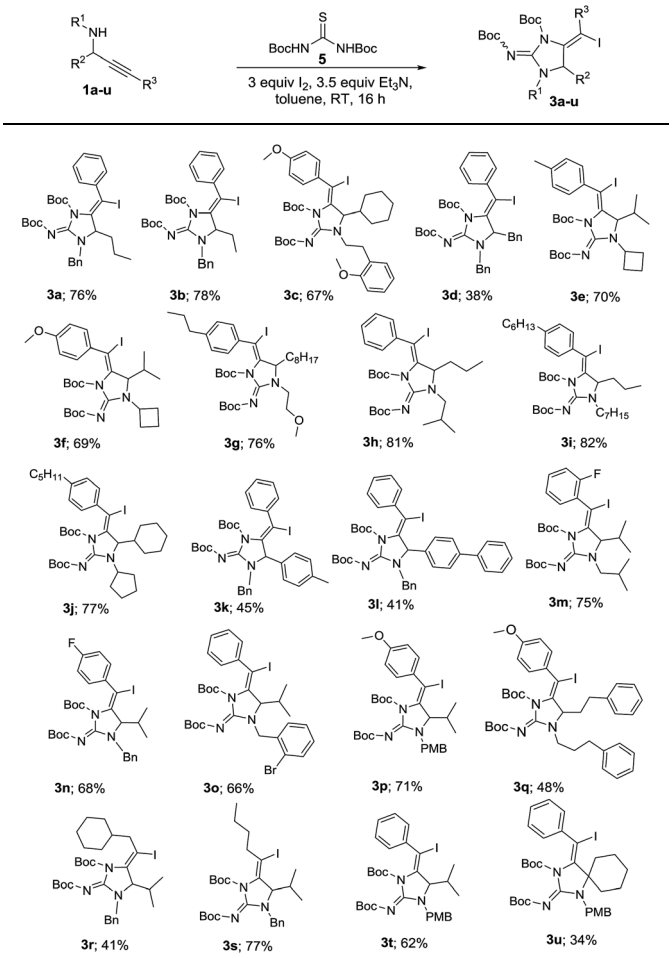
Entry	5 (equiv.)	I_2 (equiv.)	Base (equiv.)	Solvent	Time (h)	Yield[b] (%)
1	1.25	2.5	DIPEA (3.5)	DCM	24	nd
2	1.25	2.5	K_2CO_3 (3.5)	DCM	24	38
3	1.25	2.5	Et_3N (3.5)	DCM	24	45
4	1.25	2.5	Et_3N (3.5)	MeCN	24	30
5	1.25	2.5	Et_3N (3.5)	Diethylether	24	42
6	1.25	2.5	Et_3N (3.5)	Toluene	24	55
7	1.25	2.5	Et_3N (3.5)	Toluene	48	48
8	1.25	2.5	Et_3N (3.5)	Toluene	72	34
9	1.25	2.5	Et_3N (3.5)	Toluene	16	72
10	1.25	2.5	Et_3N (3.5)	Toluene	12	64
11	**1.25**	**3**	**Et_3N (3.5)**	**Toluene**	**16**	**76**
12	2	3.5	Et_3N (3.5)	Toluene	16	53
13	1.25	3	Et_3N (4.0)	Toluene	16	74

[a] **1a** (1 mmol), **5** (as mentioned), I_2 (as mentioned), base (as mentioned) in solvent (1 mL) at RT for the indicated time. [b] Isolated yields.

We decided to study the feasibility of the process by performing the reaction in two steps using **1a** as a model substrate. For this, we carried out the guanylation of **1a** with *N*,*N*′-di-Boc-protected thiourea (**5**) in the presence of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDCI; 2 equiv.) and Hünig's base (3 equiv.) to generate compound **2a** (Scheme 2, route A). Next, we studied the efficiency of iodine for the heteroannulation by attempting the cyclization of **2a** using 2.0 equiv. of I_2 and 2.2 equiv. of K_2CO_3 in dichloromethane at RT. It was observed that though the desired cyclized product **3a** was formed (TLC-monitoring), the reaction could not be completed even after 12 h. Increasing the amount of both iodine (up to 2.0 equiv.) and K_2CO_3 (up to 2.2 equiv.) improved the reaction efficiency dramatically with completion of the reaction after 3 h to provide the desired 5-*exo*-dig iodocyclized product in 88% yield. Encouraged by these results, we envisioned to perform the guanylation and cyclization as a one-pot procedure as iodine could act as an activator for *N*,*N*′-di-Boc-thiourea to generate the required carbodiimide *in situ*. The resulting guanylated propargylamine **2a** will undergo iodine-mediated cyclization resulting in the formation of the desired herein, we report a facile methodology for the regio-selective synthesis of 1,4,5-substituted 2-aminoimidazoles from propargylamines by an iodine-mediated one-iminoimidazolidine **3a** (Scheme 2, route B). We started the optimization of the one-pot reaction in DCM using *N*,*N*′-di-Boc-thiourea (1.25 equiv.), iodine (2.5 equiv.) with Hünig's base (3.5 equiv.), but no product formation was observed even after 24 h (Table 1, entry 1). Substituting Hünig's base with K_2CO_3 resulted in only 38% yield (entry 2). A slight increase in yield was observed when the reaction was run with triethylamine (entry 3). The reaction performance can be substantially enhanced upon changing the solvent from DCM to toluene (entries 4–6). Attempts to enhance the yield by increasing the reaction time resulted in a poorer yield (entries 7–8). To our great satisfaction, we found that shortening the reaction time to 16 h provided **3a** in 72% yield (entry 9), although a further reduction led to a decreased yield (entry 10). A slightly better yield could be obtained by increasing the amount of iodine to 3 equiv. (entry 11). Changing the amount of thiourea or base did not bring amelioration (entries 12 and 13). It should be mentioned that, unlike our previous report,[10e] where attempts to carry out guanylation and cyclization consecutively using *N*,*N*′-di-Boc-thiourea with silver catalyst, failed, this protocol could effectively provide the 5-*exo*-dig cyclized product.

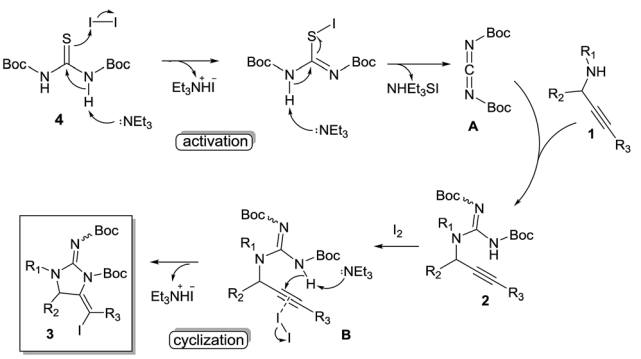
After establishing the optimized reaction conditions (Table 1, entry 11), the scope of this reaction was explored (Table 2). A small library of secondary propargylamines (**1a–u**) was generated using a variety of aldehydes, primary amines, and alkynes in the microwave-good yields. Electron-withdrawing groups as well as electron assisted A^3-coupling under our previously reported conditions.[19] They reacted smoothly to give iodo-iminoimidazolidines **3a–u** in donating groups present on the alkyne moiety were well tolerated. Similarly, the nature of the amine substituent had no significant influence on the product yield. However, the substitution arising from the aldehyde during A^3-coupling has significant effect on the product

Table 2 Scope of reaction[a,b]



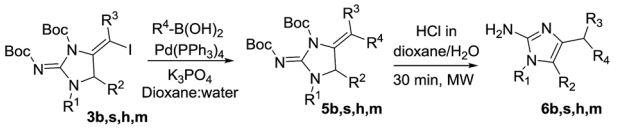
[a] **1a–u** (1 mmol), **2** (1.25 equiv.), I_2 (3 equiv.), Et_3N (3.5 equiv.) in toluene (1 mL) at RT for 16 h. [b] Isolated yields. Bn = benzyl; PMB = *p*-methoxybenzyl; Boc = *tert*-butoxycarbonyl.

formation as evident from the Table 2, where aromatic are the low yielding ones. Remarkably, this protocol was further extended to a propargylamine prepared from cyclohexanone (KA^2 coupling)[20] giving a spiro-cyclized product **3u** in moderate yield.



Scheme 3 Proposed mechanism.

Table 3 Suzuki cross-coupling[a]



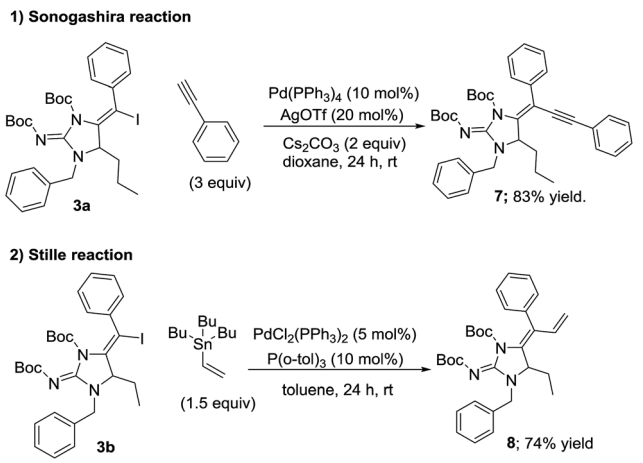
Entry	R1	R2	R3	R4	Yield of 5 (%)	Yield of 6 from 5 (%)
1	Benzyl	Ethyl	Phenyl	Phenyl	85	100
2	Benzyl	Iso-butyl	Butyl	4-Fluorophenyl	84	100
3	Iso-butyl	Propyl	Phenyl	3,5-Dimethylphenyl	62	100
4	Iso-butyl	Iso-propyl	2-Fluorophenyl	3,5-Dimethoxyphenyl	40	100

[a] **3** (1 mmol), boronic acid (1.5 equiv.), $Pd(PPh_3)_4$ (6 mol%), K_3PO_4 (2 equiv.) in dioxane : water (9 : 1) (1.5 mL) at 80 °C for 24 h. Deprotection was carried out using 150 equiv. of 4N HCl in dioxane : water under microwave irradiation at 70 °C and 100 W for 30 min.

On the basis of literature reports[16g,21] and our previous work,[10e] a plausible mechanism for the iodine-mediated heteroannulation is shown in Scheme 3. We assume that *N*,*N*′-di-Boc-thiourea upon reaction with iodine and Et_3N leads to the formation of carbodiimide **A** by thiourea desulfurization.[22] Subsequently **A** is trapped by propargylamine **1** providing the protected propargylguanidine **2**. Iodine promoted nucleophilic attack of the guanidine on the activated alkyne led to *exo*-dig cyclization affording iodo-imidazole **3** *via* intermediate **B**. It may find mention here that during the course of this study Zhou and co-workers reported the synthesis of imidazolidin-2-imine derivatives from diarylcarbodiimide and propargylamines which corroborates well with our findings.[18]

Finally, to further decorate the synthesized 2-iminoimidazolidine scaffold, the iodo group was used as a convenient synthetic handle for Pd-catalyzed coupling reactions.

Using 2-iminoimidazolidine **3b** (1 equiv.), substituted boronic acid (1.5 equiv.) in the presence of $Pd(PPh_3)_4$ (6 mol%) and K_3PO_4 (2 equiv.) in dioxane/water (9 : 1) at 80 °C for 24 h, compounds **5b** were obtained in moderate to good yields (Table 3) without the occurrence of de-iodinated side-product.



Scheme 4 Cross-coupling reactions.

Further, the above protocol was successfully extended to Sonogashira reaction of **3a** with phenyl acetylene delivering compound **7** in 83% yield (Scheme 4, entry 1). Similarly, Stille reaction between **3b** and allyltributylstannane led to the successful generation of compound **8** in 74% yield (Scheme 4, entry 2).

Conclusion

We have elaborated an efficient methodology for the direct guanylation and 5-*exo*-dig selective iodoamination of propargylamines in an one-pot fashion starting from highly functionalized secondary propargylamines. This convenient process provided the products with excellent regioselectivity and functional group tolerance without the need of expensive metal catalyst. The iodo group allows further functionalization giving a way to a rapid increase in molecular complexity of these multisubstituted 2-aminoimidazoles.

Acknowledgements

Support was provided by the Research Fund – Flanders (FWO) and the Research Fund of the University of Leuven (KU Leuven). PF is grateful to the University of Leuven (KU Leuven) for providing a doctoral fellowship and to Geert Hooyberghs for the fruitful discussions and his valuable suggestions. NS is grateful to the University of Leuven (KU Leuven) for obtaining a post-doctoral fellowship.

Notes and references

1 (*a*) H. Hoffmann and T. Lindel, *Synthesis*, 2003, 1753; (*b*) M. Steven, *Nat. Prod. Rep.*, 2007, **24**, 931; (*c*) J. D. Sullivan, R. L. Giles and R. E. Looper, *Curr. Bioact. Compd.*, 2009, **5**, 39; (*d*) A. Žula, D. Kikelj and J. Ilaš, *J. Heterocycl. Chem.*, 2015, **53**, 345.

2 M. Ilies, L. Di Costanzo, M. L. North, J. A. Scott and D. W. Christianson, *J. Med. Chem.*, 2010, **53**, 4266.

3 (*a*) M. S. Malamas, J. Erdei, I. Gunawan, K. Barnes, M. Johnson, Y. Hui, J. Turner, Y. Hu, E. Wagner, K. Fan,

A. Olland, J. Bard and A. J. Robichaud, *J. Med. Chem.*, 2009, **52**, 6314; (*b*) M. S. Malamas, J. Erdei, I. Gunawan, J. Turner, Y. Hu, E. Wagner, K. Fan, R. Chopra, A. Olland, J. Bard, S. Jacobsen, R. L. Magolda, M. Pangalos and A. J. Robichaud, *J. Med. Chem.*, 2010, **53**, 1146.

4 K. Singh, V. Verma, K. Yadav, V. Sreekanth, D. Kumara, A. Bajaj and V. Kumar, *Eur. J. Med. Chem.*, 2014, **84**, 150.

5 K. S. Atwal, S. V. O'Neil, S. Ahmad, L. Doweyko, M. Kirby, C. R. Dorso, G. Chandrasena, B. C. Chen, R. Zhao and R. Zahler, *Bioorg. Med. Chem. Lett.*, 2006, **16**, 4796.

6 M. E. Garst, C. Gluchowski, D. A. Harcourt and S. A. Munk, WO1995019968 A1, 1995.

7 (*a*) R. W. Huigens III, J. J. Richards, G. Parise, T. E. Ballard, W. Zeng, R. Deora and C. Melander, *J. Am. Chem. Soc.*, 2007, **129**, 6966; (*b*) S. A. Rogers and C. Melander, *Angew. Chem., Int. Ed.*, 2008, **47**, 5229; (*c*) T. E. Ballard, J. J. Richards, A. L. Wolf and C. Melander, *Chem.–Eur. J.*, 2008, **14**, 10745; (*d*) S. A. Rogers, R. W. Huigens, J. Cavanagh and C. Melander, *Antimicrob. Agents Chemother.*, 2010, **54**, 2112; (*e*) D. Linares, O. Bottzeck, O. Pereira, A. Praud-Tabariès and Y. Blache, *Bioorg. Med. Chem. Lett.*, 2011, **21**, 6751; (*f*) A. Yeagley, Z. Su, K. McCullough, R. Worthington and C. Melander, *Org. Biomol. Chem.*, 2013, **11**, 130; (*g*) H. Steenackers, D. S. Ermolat'ev, T. T. T. Trang, B. Savalia, U. K. Sharma, A. De Weerdt, A. Shah, J. Vanderleyden and E. V. Van der Eycken, *Org. Biomol. Chem.*, 2014, **12**, 3671.

8 R. Borman, R. Coleman, K. Clark, A. Oxford, G. Hynd, J. Archer, A. Aley and N. Harris, WO 2005012263 A1, 2005.

9 M. A. Richardson, R. E. Furlani, B. K. Podell, D. F. Ackart, J. D. Haugen, R. J. Melander, C. Melander and R. J. Basaraba, *Tetrahedron Lett.*, 2015, **56**, 3406.

10 (*a*) S. Nakamura, I. Kawasaki, M. Kunimura, M. Matsui, Y. Noma, M. Yamashita and S. Ohta, *J. Chem. Soc., Perkin Trans. 1*, 2002, 1061; (*b*) N. S. Aberle, G. Lessene and K. G. Watson, *Org. Lett.*, 2006, **8**, 419; (*c*) D. S. Ermolat'ev, V. L. Alifanov, V. B. Rybakov, E. V. Babaev and E. Van der Eycken, *Synthesis*, 2008, 2083; (*d*) P. B. Koswatta and C. J. Lovely, *Chem. Commun.*, 2010, **46**, 2148; (*e*) D. S. Ermolat'ev, J. B. Bariwal, H. P. L. Steenackers, S. C. J. De Keersmaecker and E. Van der Eycken, *Angew. Chem., Int. Ed.*, 2010, **49**, 9465; (*f*) Z. Su, L. Peng and C. Melander, *Tetrahedron Lett.*, 2012, **53**, 1204; (*g*) B. P. Zavesky, N. R. Babij and J. P. Wolfe, *Org. Lett.*, 2014, **16**, 4952; (*h*) X. Guo, W. Chen, B. Chen, W. Huang, W. Qi, G. Zhang and Y. Yu, *Org. Lett.*, 2015, **17**, 1157; (*i*) J. B. Gibbons, J. M. Salvant, R. M. Vaden, K.-H. Kwon, B. E. Welm and R. E. Looper, *J. Org. Chem.*, 2015, **80**, 10076.

11 (*a*) G. L. Eilrich and W. D. Dixon, *US*-3904395, 1975; (*b*) O. P. Pereshivko, V. A. Peshkov, D. S. Ermolat'ev, S. Van Hove, K. Van Hecke, L. Van Meervelt and E. V. Van der Eycken, *Synthesis*, 2011, **10**, 1587; (*c*) W. Jia-Jie, Y. Zhu and Z.-P. Zhan, *Asian J. Org. Chem.*, 2012, **1**, 108.

12 (*a*) W.-J. Yoo, L. Zhao and C.-J. Li, *Aldrichimica Acta*, 2011, **44**, 43; (*b*) V. A. Peshkov, O. P. Pereshivko and E. V. Van der Eycken, *Chem. Soc. Rev.*, 2012, **41**, 3790.

13 R. L. Giles, J. D. Sullivan, A. M. Steiner and R. E. Looper, *Angew. Chem., Int. Ed.*, 2009, **48**, 3116.

14 M. J. Gainer, N. R. Bennett, Y. Takahashi and R. E. Looper, *Angew. Chem., Int. Ed.*, 2011, **50**, 684.

15 (*a*) S. Das, R. Borah, R. R. Devi and A. J. Thakur, *Synlett*, 2008, **18**, 2741; (*b*) B. Alcaide, P. Almendros, G. Cabrero, R. Callejo, M. P. Ruiz, M. Arno and L. R. Domingo, *Adv. Synth. Catal.*, 2010, **352**, 1688; (*c*) W. Lee, H. Shen, W. Hu, W. Lo, C. Murali, J. K. Vandavasi and J. Wang, *Adv. Synth. Catal.*, 2012, **354**, 2218; (*d*) K. Xu, Y. Hu, S. Zhang, Z. Zha and Z. Wang, *Chem.–Eur. J.*, 2012, **18**, 9793.

16 (*a*) V. P. Mehta, S. G. Modha, D. S. Ermolat'ev, K. Van Hecke, L. Van Meervelt and E. Van der Eycken, *Aust. J. Chem.*, 2009, **62**, 27; (*b*) M. J. Mphahlele, *Molecules*, 2009, **14**, 4814; (*c*) S. Mehta and R. C. Larock, *J. Org. Chem.*, 2010, **75**, 1652; (*d*) D. Sucunza, A. Samadi, M. Chioua, D. B. Silva, C. Yunta, L. Infantes, M. C. Carreiras, E. Soriano and J. Marco-Contelles, *Chem. Commun.*, 2011, **47**, 5043; (*e*) S. K. Sharma, A. K. Mandadapu, B. Kumar and B. Kundu, *J. Org. Chem.*, 2011, **76**, 6798; (*f*) S. Li, Z. Li, Y. Yuan, D. Peng, Y. Li, L. Zhang and Y. Wu, *Org. Lett.*, 2012, **14**, 1130; (*g*) N. M. Mishra, D. D. Vachhani, S. G. Modha and E. V. Van der Eycken, *Eur. J. Org. Chem.*, 2013, 693.

17 (*a*) P. A. Donets, K. Van Hecke, L. Van Meervelt and E. V. Van der Eycken, *Org. Lett.*, 2009, **11**, 3618; (*b*) V. A. Peskov, S. Van Hove, P. A. Donets, O. P. Pereshivko, K. Van Hecke, L. Van Meervelt and E. V. Van der Eycken, *Eur. J. Org. Chem.*, 2011, 1837; (*c*) S. G. Modha, D. D. Vachhani, J. Jacobs, L. Van Meervelt and E. V. Van der Eycken, *Chem. Commun.*, 2012, **48**, 6550; (*d*) S. G. Modha, A. Kumar, D. D. Vachhani, J. Jacobs, S. K. Sharma, V. S. Parmar, L. Van Meervelt and E. V. Van der Eycken, *Angew. Chem., Int. Ed.*, 2012, **51**, 9572; (*e*) S. G. Modha, A. Kumar, D. D. Vachhani, S. K. Sharma, V. S. Parmar and E. V. Van der Eycken, *Chem. Commun.*, 2012, **48**, 10916.

18 S. Huang, Y. Shao, R. Liu and X. Zhou, *Tetrahedron*, 2015, **71**, 4219.

19 J. B. Bariwal, D. S. Ermolat'ev and E. V. Van der Eycken, *Chem.–Eur. J.*, 2010, **16**, 3281.

20 O. P. Pereshivko, V. A. Peshkov and E. V. Van der Eycken, *Org. Lett.*, 2010, **12**, 2638.

21 (*a*) S. P. Bew and D. W. Knight, *Chem. Commun.*, 1996, 1007; (*b*) G. M. M. El-Taeb, A. B. Evans, S. Jones and D. W. Knight, *Tetrahedron Lett.*, 2001, **42**, 5945; (*c*) D. W. Knight, H. C. Rost, C. M. Sharland and J. Singkhonrat, *Tetrahedron Lett.*, 2007, **48**, 7906; (*d*) S. P. Bew, G. M. M. El-Taeb, S. Jones, D. W. Knight and W.-F. Tan, *Eur. J. Org. Chem.*, 2007, **34**, 5759; (*e*) S. G. Wen, W. M. Liu and Y. M. Liang, *Synthesis*, 2007, 3295; (*f*) B. Gabriele, R. Mancuso, G. Salerno and R. C. Larock, *J. Org. Chem.*, 2012, **77**, 7640.

22 (*a*) A. R. Ali, H. Ghosh and B. K. Patel, *Tetrahedron Lett.*, 2010, **51**, 1019; (*b*) S. Resch, A.-R. Schneider, R. Beichler, M. B. M. Spera, J. Fanous, D. Schollmeyer and S. R. Waldvogel, *Eur. J. Org. Chem.*, 2015, **2015**, 933.

