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Highly enantioselective aza-Henry reaction with isatin *N*-Boc ketimines†

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A highly enantioselective aza-Henry reaction with isatin *N*-Boc ketimines using a Cu(II)–BOX complex as a catalyst is described. The reaction, which does not require protection of the N1 atom, provides the corresponding nitroamines bearing a quaternary stereocentre with high yields and enantiomeric excesses (up to 99.9%).

The nucleophilic addition of nitronate species to imine electrophiles (aza-Henry or nitro-Michael reaction) is a carbon–carbon bond-forming method of prime importance in organic synthesis.[1] This reaction leads to β-nitroamines, which are synthetically useful compounds due to the presence of two vicinal nitrogen-containing functionalities in different oxidation states, providing opportunities for selective manipulation of either.[2,3] Addition of nitrocompounds to prochiral imines gives rise to the formation of one or two new stereogenic centres. Therefore, tremendous effort has been dedicated to the development of asymmetric versions[1] of this transformation and excellent results have been obtained with aldimines through different procedures involving metal-catalysis[4] or organo-catalysis.[5] However, the catalytic enantioselective aza-Henry reaction of the less reactive ketimines, which leads to the direct formation of a quaternary stereocentre,[6] remains almost unexplored. A first example by Feng *et al.* described the addition of nitromethane to *N*-sulfonyl ketimines catalysed by a *N*,*N*′-dioxide–copper(I) complex, with fair to excellent enantioselectivities, but moderate yields.[7] Furthermore, three organocatalytic procedures involving different thiourea catalysts have been reported. Wang *et al.*[8] carried out the aza-Henry reaction with highly reactive trifluoromethyl ketimines catalysed by chiral thiourea, which was applied to the synthesis of the Anti-HIV Drug DPC 083, but that could not be extended to less reactive methyl or phenyl ketimines. More recently, Alemán *et al.*[9] have carried out the addition of nitroalkanes to 2-aryl-3*H*-indol-3-ones catalysed by thiourea–cinchona derivatives to obtain enantiomerically enriched indolin-3-ones bearing a chiral quaternary centre at the 2 position with good ee's. Finally, Dixon[10] has developed bifunctional thiourea catalysts incorporating an iminophosphorane basic moiety, which catalysed the addition of nitromethane to *N*-phosphinoyl ketimines with good yields and enantioselectivities.

The oxindole skeleton featuring a quaternary stereocentre at C3 is present in numerous naturally occurring alkaloids and pharmaceutically active compounds.[11] These compounds are attractive targets in organic synthesis due to their usefulness as drug candidates and as intermediates in alkaloid synthesis.[12] Among the various chiral oxindoles, 3-amino-2-oxindoles bearing a stereogenic centre have been recognized as key structures in a variety of biologically active compounds exhibiting significant pharmaceutical properties. A few examples are shown in Fig. 1, which include the gastrin/cholecystokinin-B receptor antagonist AG-041R,[13] the orally active vasopressin V1b receptor antagonist SSR149415,[14] or the spirooxindole anti-malarial agent NITD609.[15]

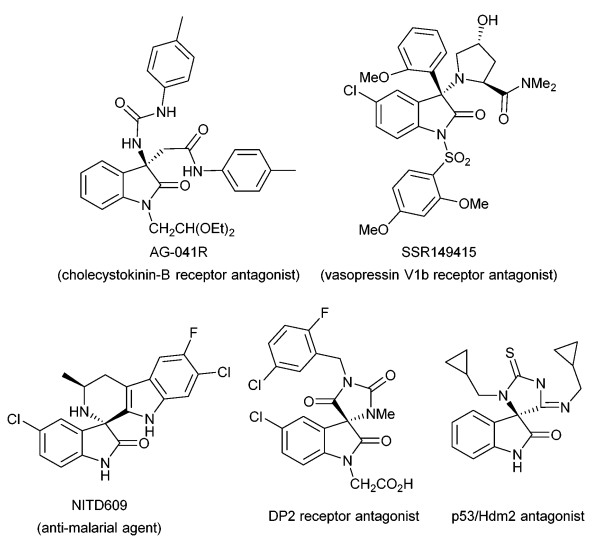

Fig. 1 Examples of biologically active 3-aminooxindoles.

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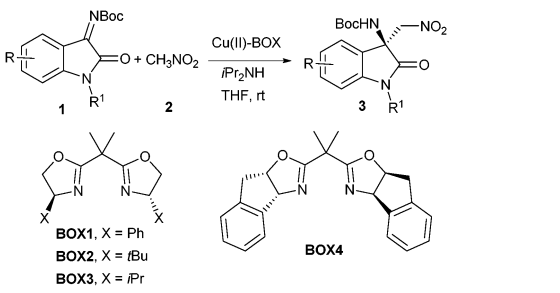
Some bioactive oxindoles feature 3,3′ spiranic moieties which incorporate two nitrogen atoms onto their cyclic structures as for instance in the DP2 receptor antagonist spirohydantoin[16] or in the spirocyclic thiourea with p53/Hdm2 antagonist activity.[17] In fact, the presence of these two nitrogen atoms is responsible for the increased potency and bioavailability of the DP2 receptor antagonist.[16b]

Because of the significance of chiral 3-amino-oxindoles in medicinal chemistry, the development of procedures for their enantioselective synthesis has received considerable attention in recent years.[18] Together with the electrophilic amination of oxindoles,[19] the asymmetric addition of carbon nucleophiles to isatin ketimines represents a straightforward procedure for the synthesis of this kind of compounds. Accordingly, examples of catalytic enantioselective Strecker,[20] Mannich,[21] Friedel–Crafts[22] and homoenolate addition[23] reactions featuring isatin imines as electrophiles have been reported in the literature. In this communication, we describe our results on the development of a highly enantioselective aza-Henry reaction with isatin ketimines (Scheme 1), a reaction that has not been explored yet to a great extent. Zhou *et al.* pioneered this work using a quinine-derived bifunctional catalyst obtaining modest to good enantioselectivities.[24] Also during the preparation of this manuscript, the enantioselective addition of nitromethane to 1-methylisatin *N*-Boc ketimines using a pyBidine-$NiCl_2$ catalyst has been reported by the group of Arai.[25]

Because of the commercial availability and high performance of bis-oxazoline (BOX) ligands in metal-mediated asymmetric reactions,[26] we used this kind of ligands combined with Cu(II) salts in our study.[27] The addition of nitromethane (**2a**) to the *N*-Boc imine of isatin (**1a**, R = R^1 = H) in the presence of 10 mol% of the **BOX1**–$Cu(OTf)_2$ complex gave a low yield (21%) of the aza-Henry product **3a** although with excellent ee (99.2%) together with 51% yield of isatin resulting from hydrolysis of the imine (Table 1, entry 1). As isatin formation could not be prevented even when performing the reaction in the presence of molecular sieves (Table 1, entry 2), we thought that this side reaction may be caused by the strongly acidic copper triflate. The use of less acidic copper(II) salts avoided imine hydrolysis but affected the enantioselectivity (Table 1, entries 1–5). The best result was obtained with copper(II) tetrafluoroborate hydrate, which allowed us to obtain compound **3a** in quantitative yield and 99.8% ee (Table 1, entry 5). The catalyst load could be reduced to 5 mol% without an appreciable effect (Table 1, entry 6). Other commercially available BOX ligands were also tested (Table 1, entries 7–9). Ligands **BOX2** and **BOX3** bearing aliphatic substituents on the oxazoline ring gave almost racemic compounds while **BOX4** gave compound **3a** with good yield and high ee.



Scheme 1 Aza-Henry reaction with isatin *N*-Boc ketimines.

Table 1 Addition of nitromethane to isatin *N*-Boc ketimine **1a** (R = R′ = H). Screening of conditions[a]

Entry	Cu(II)	BOX	3a yield (%)	ee[b] (%)
1	$Cu(OTf)_2$	**BOX1**	21 (51)[c]	99.2
2[d]	$Cu(OTf)_2$	**BOX1**	44 (20)[c]	97.0
3	$Cu(AcO)_2$	**BOX1**	97	27.0
4	$CuCl_2$	**BOX1**	98	85.0
5	$Cu(BF_4)_2{\cdot}H_2O$	**BOX1**	100	99.6
6[e]	$Cu(BF_4)_2{\cdot}H_2O$	**BOX1**	100	98.2
7	$Cu(BF_4)_2{\cdot}H_2O$	**BOX2**	98	6.0
8	$Cu(BF_4)_2{\cdot}H_2O$	**BOX3**	96	8.0
9	$Cu(BF_4)_2{\cdot}H_2O$	**BOX4**	94	−89.9

[a] Cu(II) salt (10 mol%), **BOX** (10 mol%), i-Pr_2NH (13 mol%), $MeNO_2$ (9.2 eq.), r.t. [b] Determined by HPLC with chiral stationary phases. [c] Yield of isatin in brackets. [d] Reaction carried out in the presence of 4 Å M.S. [e] $Cu(BF_4)_2$ (5 mol%), **BOX1** (5 mol%), i-Pr_2NH (7 mol%), $MeNO_2$ (9.2 eq.), r.t.

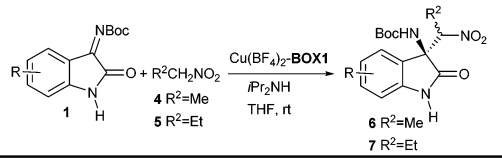
Next, the scope of the addition of nitromethane to substituted isatin ketimines was studied (Table 2). Whilst the recently reported procedures[24,25] needed isatin derivatives bearing an alkyl group at the N1-atom that makes their deprotection difficult, our method gave high yields and enantioselectivities with N1-unprotected isatin ketimines. Furthermore, better results were also obtained with N1-protected isatin ketimines, especially with those isatin derivatives having electron-withdrawing groups attached to this position. Thus, we obtained excellent results with the 1-carbamoylated imine **1e** (Table 2, entry 5) while low yield (19%) and ee (57%) have been reported for the reaction of the related 1-acetyl isatin *N*-Boc ketimine with the pyBidine-$NiCl_2$ catalyst.[25] *N*-Boc imines of isatins substituted on the aromatic ring were also suitable substrates for this reaction (Table 2, entries 6–14), which gave the corresponding *N*-Boc nitroamines **3** with good yields and excellent enantiomeric excesses above 93%, except in the cases of imine **1h** bearing a bulky bromide at the C5 position (Table 2, entry 8) and imine **1j** bearing a strong

Table 2 Addition of nitromethane to isatin *N*-Boc ketimines **1**. Scope of the reaction[a]

Entry	1	R	R^1	*t* (h)	3	Yield (%)	ee[b] (%)
1	**1a**	H	H	22	**3a**	99	99.6
2	**1b**	H	Me	16	**3b**	82 (14)[c]	99.8
3	**1c**	H	Bn	16	**3c**	79 (13)[c]	99.9
4	**1d**	H	MOM	16	**3d**	84 (14)[c]	99.9
5	**1e**	H	Boc	18	**3e**	91	99.9
6	**1f**	5-Me	H	15	**3f**	94	96.3
7	**1g**	5-MeO	H	16	**3g**	97	97.7
8	**1h**	5-Br	H	22	**3h**	95	81.3
9	**1i**	5-Cl	H	15	**3i**	87	97.5
10	**1j**	5-NO_2	H	15	**3j**	92	6.6
11[d]	**1k**	6-Cl	H	21	**3k**	92	96.2
12	**1l**	7-Cl	H	21	**3l**	94	98.1
13	**1m**	7-F	H	22	**3m**	86	93.1
14[d]	**1n**	4,7-Me_2	H	15	**3n**	89	98.7
15[e]	**1a**	H	H	22	**3a**	98	95.8

[a] **1** (0.25 mmol), $Cu(BF_4)_2$ (10 mol%), **BOX1** (10 mol%), i-Pr_2NH (13 mol%), $MeNO_2$ (9.2 eq.), r.t. [b] Determined by HPLC with chiral stationary phases. [c] Yield of the isatin nitroaldol product in brackets. [d] $Cu(BF_4)_2$ (5 mol%), **BOX1** (5 mol%), i-Pr_2NH (7 mol%), $MeNO_2$ (9.2 eq.), r.t. [e] Reaction carried out with 3.0 mmol of **1a**.

Table 3 Addition of larger nitroalkanes to isatin *N*-Boc ketimines **1**[a]



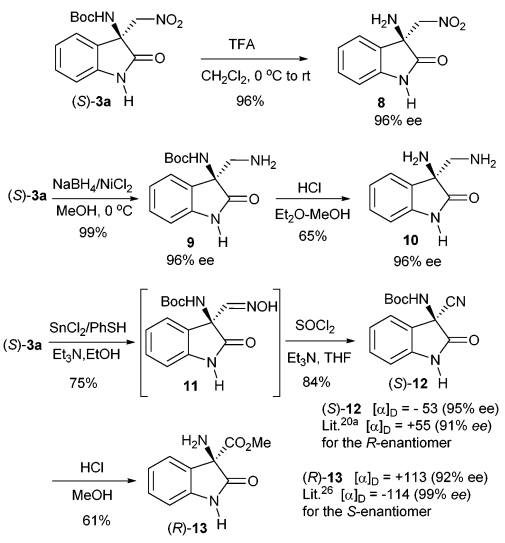
Entry	1	R	R^2	*t* (h)	6–7	Yield[b] (%)	dr[c]	ee[d] (%)
1	**1a**	H	Me	22	**6a**	68 (25)	91 : 09	99.8/99.1
2	**1a**	H	Et	16	**7a**	75 (20)	91 : 09	99.6/98.0
3	**1k**	6-Cl	Me	16	**6k**	95	60 : 40	91.7/88.8
5	**1k**	6-Cl	Et	16	**7k**	91	85 : 15	87.8/78.8
5	**1l**	7-Cl	Me	18	**6l**	91	76 : 24	98.9/99.9
6	**1l**	7-Cl	Et	15	**7l**	89	88 : 12	99.8/99.8

[a] $Cu(BF_4)_2$ (10 mol%), **BOX1** (10 mol%), i-Pr_2NH (13 mol%), $R^2CH_2NO_2$ (9.2 eq.), r.t. [b] Yield of the isatin nitroaldol product in brackets. [c] Determined by ^1H NMR. [d] Determined by HPLC with chiral stationary phases. Enantiomeric excesses for the major and minor diastereomers.

electron withdrawing nitro group at the same position (Table 2, entry 10). Remarkably, the reaction can be scaled up at least up to a 3.0 mmol scale maintaining the high yield and high enantioselectivity (Table 2, entry 15).

The results of a few examples of the aza-Henry reaction with larger nitroalkanes are provided in Table 3. Nitroethane (**4**) and nitropropane (**5**) reacted with imines **1a**, **1k**, and **1l** to give the corresponding products **6** and **7**, respectively, with good yields, fair to good diastereomeric ratios (dr), and excellent enantiomeric excesses for both diastereomers.

Some modifications of nitroamine **3a** are outlined in Scheme 2. Deprotection of the *N*-Boc amino group in compound **3a** was carried out with trifluoroacetic acid in dichloromethane at room temperature to give the free nitro amine **8** with good yield. Reduction of the nitro group was achieved with $NaBH_4/NiCl_2$ to obtain the mono-protected diamine **9** in 99% yield, which upon removal of the Boc protecting group with HCl in diethyl ether/methanol gave the free bis-amine **10** in 65% yield. On the other hand, reduction of the nitro group with $SnCl_2$ allowed obtaining 75% yield of a mixture of two



Scheme 2 Examples of functional modification of compound **3a**.

stereoisomeric oximes **11** that were dehydrated with $SOCl_2/Et_3N$ to give amino nitrile **12** in 84% yield. These kinds of compounds are useful synthetic intermediates for spirocyclic oxindoles.[28] Treatment of nitrile **12** with dry HCl in MeOH gave amino ester **13** in 61% yield with a decreased ee (92%).

The absolute stereochemistry of compounds **12** and **13** obtained in this way was achieved upon comparison of their optical rotation values and HPLC traces with those reported in the literature.[20a,28] The configuration of the quaternary stereocentre in compound **3a** was determined to be *S* by chemical correlation. For the rest of the aza-Henry products **3**, **6** and **7**, it was achieved upon the assumption of a uniform stereochemical mechanism.

In conclusion, we have developed a highly efficient procedure for the enantioselective aza-Henry reaction with isatin *N*-Boc ketimines catalysed by Cu(II)–BOX complexes. Compared with the precedents recently appeared in the literature,[24,25] our method provides higher yields and enantioselectivities (above 93% ee in most of the cases). Interestingly, the protection of the N1 atom is not required, although in our case the presence of either electron-donating or electron-withdrawing groups at this position does not affect the enantioselectivity of the reaction, making our procedure of much more general application. The use of commercially available ligands represents an additional advantage.

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Notes and references

1 (*a*) B. Westermann, *Angew. Chem., Int. Ed.*, 2003, **42**, 151; (*b*) A. Ting and S. E. Schaus, *Eur. J. Org. Chem.*, 2007, 5797; (*c*) E. Marqués-López, P. Merino, P. Tejero and R. P. Herrera, *Eur. J. Org. Chem.*, 2009, 2401; (*d*) A. Noble and J. C. Anderson, *Chem. Rev.*, 2013, **113**, 2887.

2 Synthesis of diamines: (*a*) D. Lucet, T. Le Gall and C. Mioskowski, *Angew. Chem., Int. Ed.*, 1998, **37**, 2580; (*b*) L. Bernadi, B. F. Bonini, E. Capito, G. Dessole, M. Comes-Franchini, M. Fochi and A. Ricci, *J. Org. Chem.*, 2004, **69**, 8168; (*c*) H. Zhou, D. Peng, B. Qin, Z. Hou, X. Liu and X. Feng, *J. Org. Chem.*, 2007, **72**, 10302.

3 Nef reaction: (*a*) R. Ballini and M. Petrini, *Tetrahedron*, 2004, **60**, 1017; (*b*) E. Foresti, G. Palmieri, M. Petrini and R. Profeta, *Org. Biomol. Chem.*, 2003, **1**, 4275; (*c*) C. Najera and J. M. Sansano, *Chem. Rev.*, 2007, **107**, 4584.

4 Rare earth catalyst (*a*) K. Yamada, S. J. Harwood, H. Groger and M. Shibasaki, *Angew. Chem., Int. Ed.*, 1999, **38**, 3504. Zinc catalyst (*b*) C. Palomo, M. Oiarbide, R. Halder, A. Laso and R. Lopez, *Angew. Chem., Int. Ed.*, 2005, **45**, 117. Copper catalyst (*c*) N. Nishiwaki, K. R. Knudsen, K. V. Gothelf and K. A. Jørgensen, *Angew. Chem., Int. Ed.*, 2001, **40**, 2992; (*d*) G. Blay, A. Escamilla, V. Hernández-Olmos, J. R. Pedro and A. Sanz-Marco, *Chirality*, 2012, **24**, 441. Bimetallic complexes (*e*) Z. Chen, H. Morimoto, S. Matsunaga and M. Shibasaki, *J. Am. Chem. Soc.*, 2008, **130**, 2170.

5 Urea and thiourea catalyst (*a*) T. P. Yoon and E. N. Jacobsen, *Angew. Chem., Int. Ed.*, 2005, **44**, 466; (*b*) M. T. Robak, M. Trincado and J. A. Ellman, *J. Am. Chem. Soc.*, 2007, **129**, 15110; (*c*) C. Wang, X. Dong, Z. Zhang, Z. Xue and H. Teng, *J. Am. Chem. Soc.*, 2008, **130**, 8606. PTC (*d*) B. M. Nugent and R. A. Yoder, *J. Am. Chem. Soc.*, 2004, **126**, 3418; (*e*) A. Singh and J. N. Johnston, *J. Am. Chem. Soc.*, 2008, **130**, 5866; (*f*) E. Gomez-Bengoa, A. Linden, R. Lopez, I. Mugica-Mendiola, M. Oiarbide and C. Palomo, *J. Am. Chem. Soc.*, 2008, **130**, 7955–7966. Brønsted acid (*g*) M. Rueping and A. P. Antonchick, *Org. Lett.*, 2008, **10**, 1731.

6 (*a*) P. G. Cozzi, R. Hilgraf and N. Zimmermann, *Eur. J. Org. Chem.*, 2007, 5969; (*b*) M. Bella and T. Gasperi, *Synthesis*, 2009, 1583; (*c*) O. Riant and J. Hannedouche, *Org. Biomol. Chem.*, 2007, **5**, 873; (*d*) *Quaternary Stereocenters: Challenges and Solutions for Organic Synthesis*, ed. J. Christoffers and A. Baro, Wiley-VCH, Weinheim, Germany, 2006.
7 C. Tan, X. Liu, L. Wang, J. Wang and X. Feng, *Org. Lett.*, 2008, **10**, 5305.
8 H. Xie, Y. Zhang, S. Zhang, X. Chen and W. Wang, *Angew. Chem., Int. Ed.*, 2011, **50**, 11773.
9 A. Parra, R. Alfaro, L. Marzo, A. Moreno-Carrasco, J. L. García Ruano and J. Alemán, *Chem. Commun.*, 2012, **48**, 9759.
10 M. G. Nuñez, A. J. M. Farley and D. J. Dixon, *J. Am. Chem. Soc.*, 2013, **135**, 16348.
11 (*a*) A. Ali, H. Demiray, I. Khan and A. Ikhlas, *Tetrahedron Lett.*, 2014, **55**, 369; (*b*) D. Paniagua-Vega, C. M. Cerda-Garcia-Rojas, T. Ponce-Noyola and A. C. Ramos-Valdivia, *Nat. Prod. Commun.*, 2012, **7**, 1441; (*c*) K. Wang, X.-Y. Zhou, Y.-Y. Wang, M.-M. Li, Y.-S. Li, L.-Y. Peng, X. Cheng, Y. Li, Y.-P. Wang and Q.-S. Zhao, *J. Nat. Prod.*, 2011, **74**, 12; (*d*) M. Kitajima, H. Kobayashi, N. Kogure and H. Takayama, *Tetrahedron*, 2010, **66**, 5987; (*e*) K.-H. Lim, K.-M. Sim, G.-H. Tan and T.-S. Kam, *Phytochemistry*, 2009, **70**, 1182; (*f*) S. Peddibhotla, *Curr. Bioact. Compd.*, 2009, **5**, 20.
12 (*a*) F. Zhou, Y.-L. Liu and J. Zhou, *Adv. Synth. Catal.*, 2010, **352**, 1381; (*b*) C. V. Galliford and K. A. Scheidt, *Angew. Chem., Int. Ed.*, 2007, **46**, 8748–8758; (*c*) S. Mohammadi, R. Heiran, R. P. Herrera and E. Marques-Lopez, *ChemCatChem*, 2013, **5**, 2131.
13 (*a*) M. Ochi, K. Kawasaki, H. Kataoka, Y. Uchio and H. Nishi, *Biochem. Biophys. Res. Commun.*, 2001, **283**, 1118; (*b*) N. Hara, S. Nakamura, M. Sano, R. Tamura, Y. Funahashi and N. Shibata, *Chem. – Eur. J.*, 2012, **18**, 9276.
14 (*a*) K. Bernard, S. Bogliolo and J. B. Ehrenfeld, *Br. J. Pharmacol.*, 2005, **144**, 1037; (*b*) T. Oost, G. Backfisch, S. Bhowmik, M. M. van Gaalen, H. Geneste, W. Hornberger, W. Lubisch, A. Netz, L. Unger and W. Wernet, *Bioorg. Med. Chem. Lett.*, 2011, **21**, 3828.
15 (*a*) M. Rottmann, C. McNamara, B. S. K. Yeung, M. C. S. Lee, B. Zou, B. Russell, P. Seitz, D. M. Plouffe, N. V. Dharia, J. Tan, S. B. Cohen, K. R. Spencer, G. Gonzalez-Paez, L. Lakshminarayana, A. Goh, R. Suwanarusk, T. Jegla, E. K. Schmitt, H.-P. Beck, R. Brun, F. Nosten, L. Renia, V. Dartois, T. H. Keller, D. A. Fidock, E. A. E. A. Winzeler and T. T. Diagana, *Science*, 2010, **329**, 1175; (*b*) B. K. S. Yeung, B. Zou, M. Rottmann, S. B. Lakshminarayana, S. H. Ang, S. Y. Leong, J. Tan, J. Wong, S. Keller-Maerki, C. Fischli, A. Goh, E. K. Schmitt, P. Krastel, E. Francotte, K. Kuhen, D. Plouffe, K. Henson, T. Wagner, E. A. Winzeler, F. Petersen, R. Brun, V. Dartois, T. T. Diagana and T. H. Keller, *J. Med. Chem.*, 2010, **53**, 5155.
16 (*a*) E. Bueyuekbingoel and G. Klopman, *Farmaco*, 1995, **50**, 889; (*b*) S. Crosignani, C. Jorand-Lebrun, P. Page, G. Campbell, V. Colovray, M. Missotten, Y. Humbert, C. Cleva, J.-F. Arrighi, M. Gaudet, Z. Johnson, P. Ferro and A. Chollet, *ACS Med. Chem. Lett.*, 2011, **2**, 644; (*c*) R. Pettipher and T. T. Hansel, *Drug News Perspect.*, 2008, **21**, 317.
17 A. Czarna, B. Beck, S. Srivastava, G. M. Popowicz, S. Wolf, Y. Huang, M. Bista, T. A. Holak and A. Doemling, *Angew. Chem., Int. Ed.*, 2010, **49**, 5352.
18 P. Chauhan and S. S. Chimni, *Tetrahedron: Asymmetry*, 2013, **24**, 343.
19 (*a*) Z.-Q. Qian, F. Zhou, T.-P. Du, B.-L. Wang, M. Ding, X.-L. Zhao and J. Zhou, *Chem. Commun.*, 2009, 6753; (*b*) F. Zhou, X.-P. Zeng, C. Wang, X.-L. Zhao and J. Zhou, *Chem. Commun.*, 2013, **49**, 2022.
20 (*a*) D. Wang, J. Liang, J. Feng, K. Wang, Q. Sun, L. Zhao, D. Li, W. Yan and R. Wang, *Adv. Synth. Catal.*, 2013, **355**, 548; (*b*) Y.-L. Liu and J. Zhou, *Chem. Commun.*, 2013, **49**, 4421; (*c*) Y.-L. Liu, F. Zhou, J.-J. Cao, C.-B. Ji, M. Ding and J. Zhou, *Org. Biomol. Chem.*, 2010, **8**, 3847.
21 (*a*) W. Yan, D. Wang, J. Feng, P. Li, D. Zhao and R. Wang, *Org. Lett.*, 2012, **14**, 2512; (*b*) Q.-X. Guo, Y.-W. Liu, X.-C. Li, L.-Z. Zhong and Y.-G. Peng, *J. Org. Chem.*, 2012, **77**, 3589; (*c*) N. Hara, S. Nakamura, M. Sano, R. Tamura, Y. Funahashi and N. Shibata, *Chem. – Eur. J.*, 2012, **18**, 9276.
22 (*a*) J. Feng, W. Yan, D. Wang, P. Li, Q. Sun and R. Wang, *Chem. Commun.*, 2012, **48**, 8003; (*b*) S. Duce, F. Pesciaioli, L. Gramigna, L. Bernardi, A. Mazzanti, A. Ricci, G. Bartoli and G. Bencivenni, *Adv. Synth. Catal.*, 2011, **353**, 860; (*c*) J. J. Badillo, A. Silva-Garcia, B. H. Shupe, J. C. Fettinger and A. K. Franz, *Tetrahedron Lett.*, 2011, **52**, 5550.
23 (*a*) B. Zhang, P. Feng, L.-H. Sun, Y. Cui, S. Ye and N. Jiao, *Chem. – Eur. J.*, 2012, **18**, 9198; (*b*) H. Lv, B. Tiwari, J. Mo, C. Xing and Y. R. Chi, *Org. Lett.*, 2012, **14**, 5412.
24 (*a*) Y.-H. Wang, Y.-L. Liu, Z.-Y. Cao and J. Zhou, *Asian J. Org. Chem.*, 2014, **3**, 429; (*b*) Y.-H. Wang, Z.-Y. Cao, Y. Niu, X. Zhao and J. Zhou, *Acta Chim. Sin.*, 2014, **72**, DOI: 10.6023/A14040335.
25 T. Arai, E. Matsumura and H. Masu, *Org. Lett.*, 2014, **16**, 2768.
26 G. Desimoni, G. Faita and K. A. Jørgensen, *Chem. Rev.*, 2006, **106**, 3561.
27 M. Holmquist, G. Blay, M. C. Muñoz and J. R. Pedro, *Org. Lett.*, 2014, **16**, 1204.
28 A. Sacchetti, A. Silvani, F. G. Gatti, G. Lesma, T. Pilati and B. Trucchi, *Org. Biomol. Chem.*, 2011, **9**, 5515.

