Organocatalysis

International Edition: DOI: 10.1002/anie.201503844
German Edition: DOI: 10.1002/ange.201503844

Enantioselective Synthesis of Quaternary Carbon Stereocenters: Addition of 3-Substituted Oxindoles to Vinyl Sulfone Catalyzed by Pentanidiums**

*Lili Zong, Shubo Du, Kek Foo Chin, Chao Wang, and Choon-Hong Tan**

Abstract: *A pentanidium-catalyzed highly enantioselective conjugate addition of 3-alkyloxindoles to phenyl vinyl sulfone has been demonstrated. This approach allows the construction of 3,3-dialkyl-substituted oxindole frameworks with high yield and excellent enantioselectivity (up to 99%) under simple phase-transfer conditions. A variety of oxindoles bearing all-carbon quaternary stereogenic centers were obtained in the presence of 0.25 mol% pentanidium. Meanwhile, practicality was illustrated by a gram-scale asymmetric synthesis of two 3,3-dialkyl-substituted oxindoles. The resulting adduct can be smoothly transformed to the natural product analogue in a short synthetic route.*

Construction of small molecules bearing carbon atoms bonded to four distinct carbon substituents remains a long-standing challenge to catalytic enantioselective processes due to the congested nature of quaternary carbons.[1] Such important structural motif can be commonly found in many natural products. Molecules incorporating quaternary stereocenters have promising applications in pharmaceuticals, agrochemicals, and other areas.[2] During the last two decades, impressive progress in the enantioselective generation of quaternary stereogenic carbon centers has been achieved using asymmetric catalysis. Among them, the catalytic enantioselective synthesis of bioactive oxindole alkaloids[3] (Figure 1) bearing a 3-position quaternary carbon stereocenter has attracted increasing attention due to their important and extensive applications.[4] Specifically, the direct functionalization of 3-substituted oxindole by Michael reaction with activated alkenes is an attractive strategy.[5]

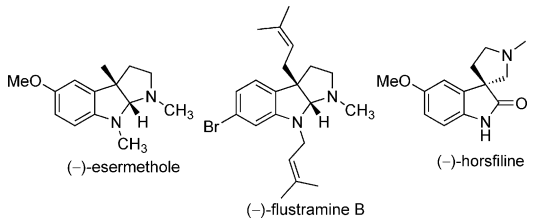


Figure 1. Bioactive oxindole alkaloid derivatives.

Vinyl sulfones are conjugate addition acceptors that are easily available from commercial sources.[6] The reaction adducts with the sulfone moiety are also versatile compounds with wide synthetic applicability by offering access to different functionalities.[7] Recently, successful attempts toward the catalytic asymmetric Michael addition of vinyl sulfone or vinyl bis(sulfone) to 3-aryl- or 3-alkyl-substituted oxindoles have been reported using organocatalysis, albeit with rather high catalyst loading of about 20 mol%.[5c,h,6f,8] Among these works, there are limited examples of highly enantioenriched 3,3-dialkyl-substituted oxindoles.[4l,8a] Therefore, further development of an approach with low catalyst loading, easy accessibility of catalyst, and broad substrate scope remains in demand.

Recently, our group has developed several structurally novel pentanidiums[9] as efficient phase-transfer catalysts[10] for asymmetric transformations. To further investigate the application of pentanidiums, variations of the catalyst are prepared and their behavior is examined in a variety of reactions. Herein, we report the highly enantioselective conjugate addition of 3-alkyloxindoles to phenyl vinyl sulfone catalyzed by previously unreported pentanidiums (Figure 2, **1b**–**e**).

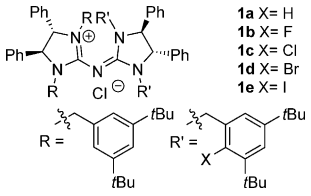


Figure 2. Various pentanidium salts.

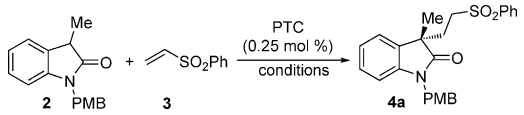
We began our investigation using pentanidium **1a** as the catalyst for conjugate addition of oxindole **2** to phenyl vinyl sulfone **3** (Table 1). The initial attempt was performed with 0.25 mol% of **1a** and K_2CO_3 as solid powder in toluene, providing the desired Michael adduct **4a** in moderate enantioselectivity of 47% (Table 1, entry 1). Encouraged by this result, we explored numerous reaction parameters such as base, solvent, temperature, and pentanidium species to improve the stereoselectivity. It was found that K_3PO_4 powder was a more appropriate choice of base in terms of reaction rate and enantioselectivity (Table 1, entry 3). Further investigation led to the discovery of cyclopentyl methyl ether (CPME) as the best solvent for improving enantioselectivity

[*] Dr. L. Zong, S. Du, K. F. Chin, Dr. C. Wang, Prof. Dr. C.-H. Tan
Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University
21 Nanyang Link, Singapore 637371 (Singapore)
E-mail: choonhong@ntu.edu.sg

[**] We gratefully acknowledge the financial support by grants from NTU (M4080946.110 and RG 6/12 M40110018.110).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201503844.

Table 1: Optimization.[a]



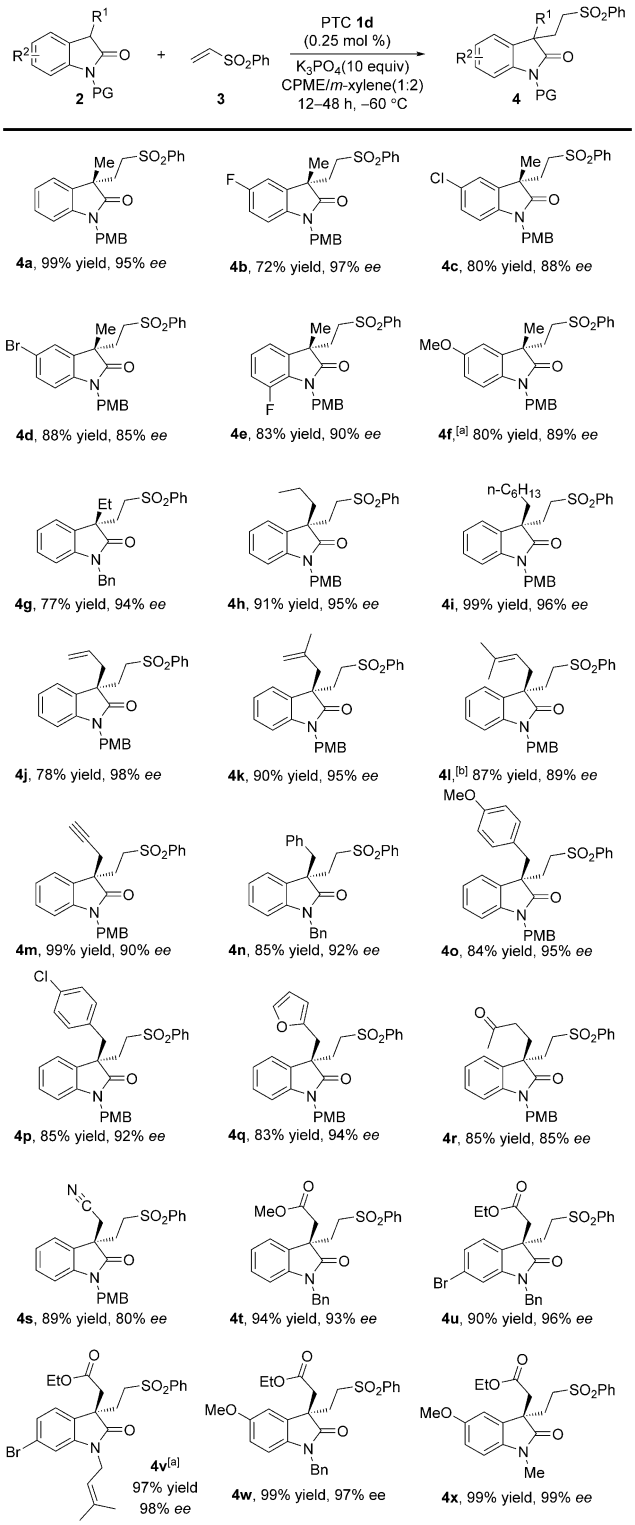
	Cat.	Base [*x* equiv]	Solvent	*T* [°C]	*t* [h]	Yield [%][b]	*ee* [%][c]
1	**1a**	K_2CO_3(5)	toluene	rt	4	80	47
2	**1a**	Cs_2CO_3(5)	toluene	rt	24	90	51
3	**1a**	K_3PO_4(5)	toluene	rt	1	90	54
4	**1a**	K_3PO_4(5)	toluene	−20	24	76	63
5	**1a**	K_3PO_4(5)	*m*-xylene	−20	24	70	68
6	**1a**	K_3PO_4(5)	MTBE	−20	24	53	50
7	**1a**	K_3PO_4(5)	CPME	−20	24	75	68
8	**1a**	K_3PO_4(10)	CPME	−40	24	85	73
9	**1a**	K_3PO_4(10)	CPME	−60	24	80	76
10	**1b**	K_3PO_4(10)	CPME	−60	24	84	78
11	**1c**	K_3PO_4(10)	CPME	−60	24	78	80
12	**1d**	K_3PO_4(10)	CPME	−60	24	80	83
13	**1d**	K_3PO_4(10)	CPME/*m*-xylene (1:2)	−60	48	80	90
14	**1e**	K_3PO_4(10)	CPME	−60	24	85	90

[a] Reactions were performed with **2** (0.02 mmol) and phenyl vinyl sulfone **3** (0.024 mmol) in the presence of 0.25 mol% pentanidium **1** with inorganic base in 0.4 mL of organic solvent. [b] Yield of isolated product. [c] Determined by HPLC analysis. The absolute configuration of **4a** was assigned to be *S* by single-crystal X-ray diffraction of **4t**. MTBE = methyl *tert*-butyl ether; PTC = pentanidium.

(entries 4–7). Overall, a moderate level of enantioselectivity was obtained using pentanidium **1a** as catalyst (entry 9). Gratifyingly, by installing different halogens to the two benzyl R groups on the pentanidium structure, improvement in enantioselectivity was achieved and a high level of enantiocontrol was obtained with brominated pentanidium **1d** or iodinated pentanidium **1e**, providing 3,3-dialkyl-substituted oxindole **4a** with 90% *ee* (entries 13–14). It is noteworthy that pentanidiums with four halogenated benzyl R groups would lead to unsatisfactory outcomes in terms of reaction rate and stereocontrol.[9c]

The substrate scope was explored by using the brominated pentanidium **1d** due to the relative ease of preparation compared with iodinated pentanidium **1e**. With 0.25 mol% of pentanidium **1d**, the reaction between a variety of 3-alkyl-substituted oxindoles and phenyl vinyl sulfone proceeded smoothly to afford the corresponding Michael adducts in good yields and excellent enantioselectivities (Scheme 1). Generally, the reaction can be completed within two days (12–48 h).[5c,8b]

Compared with 3-aryl-substituted oxindoles, 3-alkyl-substituted oxindoles, especially 3-methyloxindole is less successful when employed in the enantioselective organocatalytic Michael addition.[5b,c,f,8b,11] However, with this methodology, both the presence of either electron-withdrawing or electron-donating groups on the aromatic rings is well tolerated (**4a–f**). Meanwhile, the new phase-transfer methodology is also effective for other 3-alkyl-substituted oxindoles with longer aliphatic chain (**4g–i**) as well as oxindoles bearing allylic and propargylic substituents (**4j–m**). Moreover, adducts (**4n–q**) bearing benzyl or furan-2-ylmethyl groups



Scheme 1. Substrate scope. Conditions: reactions were performed with **2** (0.05 mmol) and phenyl vinyl sulfone **3** (0.06 mmol) in the presence of 0.25 mol% of pentanidium **1d** with 10 equivalent of powder K_3PO_4 in a solvent mixture of CPME and *m*-xylene (1:2, 1 mL) at −60°C. [a] The reaction was conducted at −40°C. [b] The reaction was conducted at −20°C. CPME = cyclopentyl methylether.

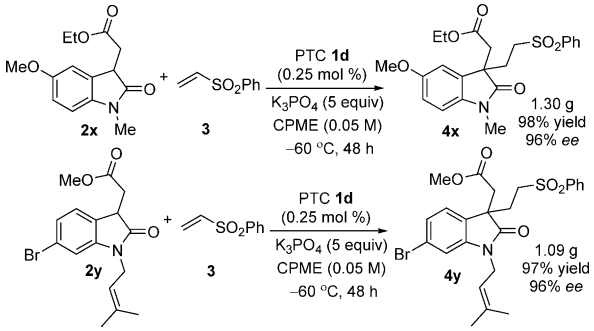
were also achieved. Aiming to expand the synthetic applicability of this transformation, more functional groups such as

ketone, nitrile, and ester are introduced into the substrate. To our delight, substrates with an ester group can smoothly undergo Michael addition to afford the desired adducts with different substitution on the aromatic ring (**4t–x**) in excellent enantioselectivity. Adducts containing ketone or nitrile were produced, however, with slightly lower enantioselectivities (**4r–s**). In most cases, the corresponding adducts can be efficiently obtained within a reasonable time at −60 °C. However, due to the electronic or steric effect of substituents, the reaction temperatures of certain substrates were raised without sacrificing the enantioselectivities (**4f**, **4l**, and **4v**). As far as we are aware, this approach provides an efficient way to synthesize the widest range of 3,3-dialkyl-substituted oxindoles bearing a quaternary carbon stereocenter with very low catalyst loading (0.25 mol%).[9a,c,12]

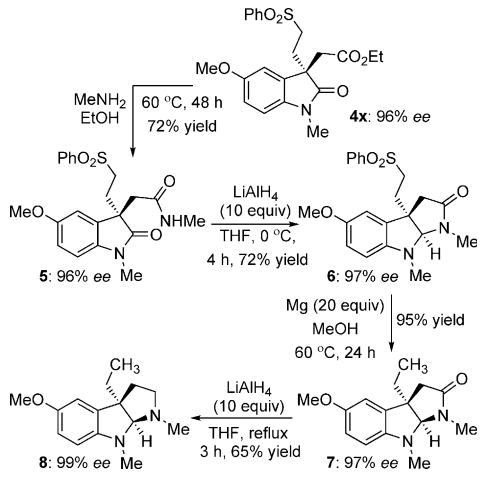
The absolute configuration of product **4t** was confirmed to be *S* using single-crystal X-ray diffraction; thus, the absolute configuration of all adducts was assigned by analogy to **4t**. Furthermore, the pentanidium phase-transfer-catalyzed Michael addition can be easily scaled up, yielding gram quantities of **4x** and **4y** in excellent yields (Scheme 2). Oxindole compounds **4x** and **4y** were obtained with an enantioselectivity of 96% *ee* and in yields of 98% and 97%, respectively.

To further illustrate the synthetic utility of the adducts such as **4x**,[7] it is transformed to an analogue of the natural product precursor esermethole (Scheme 3).[3h,13] Amidation of adduct **4x** to amide **5** went smoothly using $MeNH_2$. This is followed by reductive cyclization using $LiAlH_4$ to furnish lactam **6**. Subsequent reductive desulfonylation[8b,14] mediated by magnesium gave pyrroloindoline **7** with an ethyl junction in a high yield and without erosion of enantioselectivity. Reduction of **7** using $LiAlH_4$ in refluxing THF led to the construction of pyrroloindoline **8**, an analogue of esermethole.[15] It is noteworthy that the attempt to achieve desulfonylation of **4x** was not successful (see the Supporting Information).

In conclusion, we have described a highly enantioselective conjugate addition of 3-alkyl-substituted oxindoles with inexpensive phenyl vinyl sulfone. A broad substrate scope was achieved with pentanidium as the phase-transfer catalyst. The scalability (gram scale) and high efficiency (0.25 mol% loading of catalyst) of this reaction reveals the practical potential of this methodology. A variety of enantioenriched oxindoles containing quaternary carbon stereocenters have been obtained, which are potentially bioactive molecules and core structures for diversity-oriented functionalization. Specifically, an asymmetric synthesis of the core structure of pyrroloindoline derivatives[16] has been efficiently achieved within several synthetic steps. Mechanistic insights into chiral induction and high activity of pentanidiums in this reaction are currently ongoing.



Scheme 2. Gram-scale synthesis of 3,3-dialkyl-substituted oxindoles.



Scheme 3. Synthetic transformation of Michael addition adduct **4x**.

Keywords: conjugate addition · organocatalysis · pentanidium · quaternary carbon stereocenter · sulfones

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 9390–9393
Angew. Chem. **2015**, *127*, 9522–9525

[1] a) E. J. Corey, A. Guzman-Perez, *Angew. Chem. Int. Ed.* **1998**, *37*, 388–401; *Angew. Chem.* **1998**, *110*, 402–415; b) K. W. Quasdorf, L. E. Overman, *Nature* **2014**, *516*, 181–191; c) C. J. Douglas, L. E. Overman, *Proc. Natl. Acad. Sci. USA* **2004**, *101*, 5363–5367; d) T.-S. Mei, H. H. Patel, M. S. Sigman, *Nature* **2014**, *508*, 340–344.

[2] a) B. M. Trost, C. Jiang, *Synthesis* **2006**, 369–396; b) A. H. Mermerian, G. C. Fu, *J. Am. Chem. Soc.* **2005**, *127*, 5604–5607; c) T. Buyck, Q. Wang, J. Zhu, *Angew. Chem. Int. Ed.* **2013**, *52*, 12714–12718; *Angew. Chem.* **2013**, *125*, 12946–12950.

[3] a) P. L. Julian, J. Pikl, *J. Am. Chem. Soc.* **1935**, *57*, 755–757; b) P. L. Julian, J. Pikl, *J. Am. Chem. Soc.* **1935**, *57*, 539–544; c) T. B. K. Lee, G. S. K. Wong, *J. Org. Chem.* **1991**, *56*, 872–875; d) B. M. Trost, Y. Zhang, *J. Am. Chem. Soc.* **2006**, *128*, 4590–4591; e) M. G. Kulkarni, A. P. Dhondge, A. S. Borhade, D. D. Gaikwad, S. W. Chavhan, Y. B. Shaikh, V. B. Ningdale, M. P. Desai, D. R. Birhade, M. P. Shinde, *Tetrahedron Lett.* **2009**, *50*, 2411–2413; f) J. Liu, T. Ng, Z. Rui, O. Ad, W. Zhang, *Angew. Chem. Int. Ed.* **2014**, *53*, 136–139; *Angew. Chem.* **2014**, *126*, 140–143; g) J. F. Austin, S.-G. Kim, C. J. Sinz, W.-J. Xiao, D. W. C. MacMillan, *Proc. Natl. Acad. Sci. USA* **2004**, *101*, 5482–5487; h) T. Kawasaki, M. Shinada, D. Kamimura, M. Ohzono, A. Ogawa, *Chem. Commun.* **2006**, 420–422; i) B. M. Trost, S. Malhotra, W. H. Chan, *J. Am. Chem. Soc.* **2011**, *133*, 7328–7331; j) A. Jossang, P. Jossang, H. A. Hadi, T. Sevenet, B. Bodo, *J. Org. Chem.* **1991**, *56*, 6527–6530; k) B. M. Trost, M. K. Brennan, *Org. Lett.* **2006**, *8*, 2027–2030; l) S. Hong, M. Jung, Y. Park, M. W. Ha, C. Park, M. Lee, H.-g. Park, *Chem. Eur. J.* **2013**, *19*, 9599–9605.

[4] a) B. M. Trost, M. K. Brennan, *Synthesis* **2009**, 3003–3025; b) F. Zhou, Y.-L. Liu, J. Zhou, *Adv. Synth. Catal.* **2010**, *352*, 1381–

1407; c) P. Ruiz-Sanchis, S. A. Savina, F. Albericio, M. Álvarez, *Chem. Eur. J.* **2011**, *17*, 1388 – 1408; d) R. Dalpozzo, G. Bartoli, G. Bencivenni, *Chem. Soc. Rev.* **2012**, *41*, 7247 – 7290; e) I. D. Hills, G. C. Fu, *Angew. Chem. Int. Ed.* **2003**, *42*, 3921 – 3924; *Angew. Chem.* **2003**, *115*, 4051 – 4054; f) B. M. Trost, J. Quancard, *J. Am. Chem. Soc.* **2006**, *128*, 6314 – 6315; g) B. M. Trost, Y. Zhang, *J. Am. Chem. Soc.* **2007**, *129*, 14548 – 14549; h) S. Ma, X. Han, S. Krishnan, S. C. Virgil, B. M. Stoltz, *Angew. Chem. Int. Ed.* **2009**, *48*, 8037 – 8041; *Angew. Chem.* **2009**, *121*, 8181 – 8185; i) B. M. Trost, L. C. Czabaniuk, *J. Am. Chem. Soc.* **2010**, *132*, 15534 – 15536; j) K. Foo, T. Newhouse, I. Mori, H. Takayama, P. S. Baran, *Angew. Chem. Int. Ed.* **2011**, *50*, 2716 – 2719; *Angew. Chem.* **2011**, *123*, 2768 – 2771; k) S. B. Jones, B. Simmons, A. Mastracchio, D. W. C. MacMillan, *Nature* **2011**, *475*, 183 – 188; l) K. Ohmatsu, M. Kiyokawa, T. Ooi, *J. Am. Chem. Soc.* **2011**, *133*, 1307 – 1309; m) C. Guo, J. Song, J.-Z. Huang, P.-H. Chen, S.-W. Luo, L.-Z. Gong, *Angew. Chem. Int. Ed.* **2012**, *51*, 1046 – 1050; *Angew. Chem.* **2012**, *124*, 1070 – 1074; n) B. M. Trost, D. A. Bringley, T. Zhang, N. Cramer, *J. Am. Chem. Soc.* **2013**, *135*, 16720 – 16735; o) S. Shirakawa, K. Koga, T. Tokuda, K. Yamamoto, K. Maruoka, *Angew. Chem. Int. Ed.* **2014**, *53*, 6220 – 6223; *Angew. Chem.* **2014**, *126*, 6334 – 6337.

[5] a) R. He, C. Ding, K. Maruoka, *Angew. Chem. Int. Ed.* **2009**, *48*, 4559 – 4561; *Angew. Chem.* **2009**, *121*, 4629 – 4631; b) X. Li, B. Zhang, Z.-G. Xi, S. Luo, J.-P. Cheng, *Adv. Synth. Catal.* **2010**, *352*, 416 – 424; c) X. Li, Z.-G. Xi, S. Luo, J.-P. Cheng, *Org. Biomol. Chem.* **2010**, *8*, 77 – 82; d) M. Ding, F. Zhou, Y.-L. Liu, C.-H. Wang, X.-L. Zhao, J. Zhou, *Chem. Sci.* **2011**, *2*, 2035 – 2039; e) X.-L. Liu, Z.-J. Wu, X.-L. Du, X.-M. Zhang, W.-C. Yuan, *J. Org. Chem.* **2011**, *76*, 4008 – 4017; f) T. Zhang, L. Cheng, S. Hameed, L. Liu, D. Wang, Y.-J. Chen, *Chem. Commun.* **2011**, *47*, 6644 – 6646; g) W. Yang, J. Wang, D.-M. Du, *Tetrahedron: Asymmetry* **2012**, *23*, 972 – 980; h) H. J. Lee, S. B. Woo, D. Y. Kim, *Molecules* **2012**, *17*, 7523 – 7532; i) C. Yang, W. Chen, W. Yang, B. Zhu, L. Yan, C.-H. Tan, Z. Jiang, *Chem. Asian J.* **2013**, *8*, 2960 – 2964; j) L. Chen, Y. You, M.-L. Zhang, J.-q. Zhao, J. Zuo, X.-M. Zhang, W.-C. Yuan, X.-Y. Xu, *Org. Biomol. Chem.* **2015**; k) W.-Y. Siau, W. Li, F. Xue, Q. Ren, M. Wu, S. Sun, H. Guo, X. Jiang, J. Wang, *Chem. Eur. J.* **2012**, *18*, 9491 – 9495.

[6] a) J. J. Chen, C. V. Lu, R. N. Brockman, *Tetrahedron Lett.* **2003**, *44*, 3459 – 3462; b) H. Li, J. Song, X. Liu, L. Deng, *J. Am. Chem. Soc.* **2005**, *127*, 8948 – 8949; c) S. Mossé, A. Alexakis, *Org. Lett.* **2005**, *7*, 4361 – 4364; d) Q. Zhu, L. Cheng, Y. Lu, *Chem. Commun.* **2008**, 6315 – 6317; e) Q. Zhu, Y. Lu, *Aust. J. Chem.* **2009**, *62*, 951 – 955; f) S. Sulzer-Mossé, A. Alexakis, J. Mareda, G. Bollot, G. Bernardinelli, Y. Filinchuk, *Chem. Eur. J.* **2009**, *15*, 3204 – 3220; g) J. Xiao, Y.-L. Liu, T.-P. Loh, *Synlett* **2010**, 2029 – 2032; h) J. J. Murphy, A. Quintard, P. McArdle, A. Alexakis, J. C. Stephens, *Angew. Chem. Int. Ed.* **2011**, *50*, 5095 – 5098; *Angew. Chem.* **2011**, *123*, 5201 – 5204; i) J. Xiao, Y.-P. Lu, Y.-L. Liu, P.-S. Wong, T.-P. Loh, *Org. Lett.* **2011**, *13*, 876 – 879; j) D. C. Meadows, J. Gervay-Hague, *Med. Res. Rev.* **2006**, *26*, 793 – 814; k) P. L. Fuchs, T. F. Braish, *Chem. Rev.* **1986**, *86*, 903 – 917; l) Q. Zhu, Y. Lu, *Org. Lett.* **2009**, *11*, 1721 – 1724; m) Q. Zhu, Y. Lu, *Chem. Commun.* **2010**, *46*, 2235 – 2237.

[7] M. Nielsen, C. B. Jacobsen, N. Holub, M. W. Paixão, K. A. Jørgensen, *Angew. Chem. Int. Ed.* **2010**, *49*, 2668 – 2679; *Angew. Chem.* **2010**, *122*, 2726 – 2738.

[8] a) Q. Zhu, Y. Lu, *Angew. Chem. Int. Ed.* **2010**, *49*, 7753 – 7756; *Angew. Chem.* **2010**, *122*, 7919 – 7922; b) M. X. Zhao, W. H. Tang, M. X. Chen, D. K. Wei, T. L. Dai, M. Shi, *Eur. J. Org. Chem.* **2011**, 6078 – 6084.

[9] a) T. Ma, X. Fu, C. W. Kee, L. Zong, Y. Pan, K.-W. Huang, C.-H. Tan, *J. Am. Chem. Soc.* **2011**, *133*, 2828 – 2831; b) Y. Y. Yang, F. Moinodeen, W. Chin, T. Ma, Z. Y. Jiang, C.-H. Tan, *Org. Lett.* **2012**, *14*, 4762 – 4765; c) L. Zong, X. Ban, C. W. Kee, C.-H. Tan, *Angew. Chem. Int. Ed.* **2014**, *53*, 11849 – 11853; *Angew. Chem.* **2014**, *126*, 12043 – 12047.

[10] a) C. M. Starks, C. L. Liotta, M. Halpern, *Phase-Transfer Catalysis: fundamentals, applications, and industrial perspectives*, Chapman & Hall, New York, **1934**; b) A. Brändström, *Adv. Phys. Org. Chem.* **1978**, *15*, 267 – 330; c) T. Hashimoto, K. Maruoka, *Chem. Rev.* **2007**, *107*, 5656 – 5682; d) T. Ooi, K. Maruoka, *Angew. Chem. Int. Ed.* **2007**, *46*, 4222 – 4266; *Angew. Chem.* **2007**, *119*, 4300 – 4345; e) K. Maruoka, *Asymmetric Phase Transfer Catalysis*, Wiley-VCH, Weinheim, **2008**; f) S. Shirakawa, K. Maruoka, *Angew. Chem. Int. Ed.* **2013**, *52*, 4312 – 4348; *Angew. Chem.* **2013**, *125*, 4408 – 4445; g) K. Brak, E. N. Jacobsen, *Angew. Chem. Int. Ed.* **2013**, *52*, 534 – 561; *Angew. Chem.* **2013**, *125*, 558 – 588; h) C. Carter, S. Fletcher, A. Nelson, *Tetrahedron: Asymmetry* **2003**, *14*, 1995 – 2004; i) J. Lacour, V. Hebbe-Viton, *Chem. Soc. Rev.* **2003**, *32*, 373 – 382; j) S. C. Pan, B. List, in *Organocatalysis, Vol. 2007/2* (Eds.: M. T. Reetz, B. List, S. Jaroch, H. Weinmann), Springer, Berlin, Heidelberg, **2008**, pp. 259 – 300; k) R. J. Phipps, G. L. Hamilton, F. D. Toste, *Nat. Chem.* **2012**, *4*, 603 – 614.

[11] a) T. Bui, S. Syed, C. F. Barbas, *J. Am. Chem. Soc.* **2009**, *131*, 8758 – 8759; b) P. Galzerano, G. Bencivenni, F. Pesciaioli, A. Mazzanti, B. Giannichi, L. Sambri, G. Bartoli, P. Melchiorre, *Chem. Eur. J.* **2009**, *15*, 7846 – 7849; c) R. He, S. Shirakawa, K. Maruoka, *J. Am. Chem. Soc.* **2009**, *131*, 16620 – 16621.

[12] a) F. Giacalone, M. Gruttadauria, P. Agrigento, R. Noto, *Chem. Soc. Rev.* **2012**, *41*, 2406 – 2447; b) S. Shirakawa, K. Maruoka, *Tetrahedron Lett.* **2014**, *55*, 3833 – 3839; c) Y. Yuan, X. Zhang, K. Ding, *Angew. Chem. Int. Ed.* **2003**, *42*, 5478 – 5480; *Angew. Chem.* **2003**, *115*, 5636 – 5638; d) M. Rueping, A. P. Antonchick, T. Theissmann, *Angew. Chem. Int. Ed.* **2006**, *45*, 6751 – 6755; *Angew. Chem.* **2006**, *118*, 6903 – 6907; e) G. Rulli, N. Duangdee, K. Baer, W. Hummel, A. Berkessel, H. Gröger, *Angew. Chem. Int. Ed.* **2011**, *50*, 7944 – 7947; *Angew. Chem.* **2011**, *123*, 8092 – 8095; f) L. Wang, S. Shirakawa, K. Maruoka, *Angew. Chem. Int. Ed.* **2011**, *50*, 5327 – 5330; *Angew. Chem.* **2011**, *123*, 5439 – 5442; g) A. E. Sheshenev, E. V. Boltukhina, A. J. P. White, K. K. Hii, *Angew. Chem. Int. Ed.* **2013**, *52*, 6988 – 6991; *Angew. Chem.* **2013**, *125*, 7126 – 7129; h) S. Chandrasekhar, C. P. Kumar, T. P. Kumar, K. Haribabu, B. Jagadeesh, J. K. Lakshmi, P. S. Mainkar, *RSC Adv.* **2014**, *4*, 30325 – 30331.

[13] a) T. Kawasaki, A. Ogawa, R. Terashima, T. Saheki, N. Ban, H. Sekiguchi, K.-e. Sakaguchi, M. Sakamoto, *J. Org. Chem.* **2005**, *70*, 2957 – 2966; b) M. S. Morales-Ríos, E. Rivera-Becerril, P. Joseph-Nathan, *Tetrahedron: Asymmetry* **2005**, *16*, 2493 – 2499; c) K. Aikawa, S. Mimura, Y. Numata, K. Mikami, *Eur. J. Org. Chem.* **2011**, *2011*, 62 – 65; d) N. Hara, S. Nakamura, Y. Funahashi, N. Shibata, *Adv. Synth. Catal.* **2011**, *353*, 2976 – 2980; e) W. Chen, W. Yang, L. Yan, C.-H. Tan, Z. Jiang, *Chem. Commun.* **2013**, *49*, 9854 – 9856; f) R. Liu, J. Zhang, *Chem. Eur. J.* **2013**, *19*, 7319 – 7323; g) H. Miyamoto, T. Hirano, Y. Okawa, A. Nakazaki, S. Kobayashi, *Tetrahedron* **2013**, *69*, 9481 – 9493.

[14] a) A. C. Brown, L. A. Carpino, *J. Org. Chem.* **1985**, *50*, 1749 – 1750; b) G. H. Lee, I. K. Youn, E. B. Choi, H. K. Lee, G. H. Yon, H. C. Yang, C. S. Pak, *Curr. Org. Chem.* **2004**, *8*, 1263 – 1287.

[15] M. Pallavicini, E. Valoti, L. Villa, I. Resta, *Tetrahedron: Asymmetry* **1994**, *5*, 363 – 370.

[16] a) U. Anthoni, C. Christophersen, P. H. Nielsen, in *Alkaloids: Chemical and Biological Perspectives, Vol. 13* (Ed.: S. W. Pelletier), Pergamon, Oxford, **1999**, pp. 163 – 236; b) A. Steven, L. E. Overman, *Angew. Chem. Int. Ed.* **2007**, *46*, 5488 – 5508; *Angew. Chem.* **2007**, *119*, 5584 – 5605.

Received: April 27, 2015
Revised: May 25, 2015
Published online: July 14, 2015

