

Asymmetric Auto-Tandem Catalysis with a Planar-Chiral Ruthenium Complex: Sequential Allylic Amidation and Atom-Transfer Radical Cyclization**

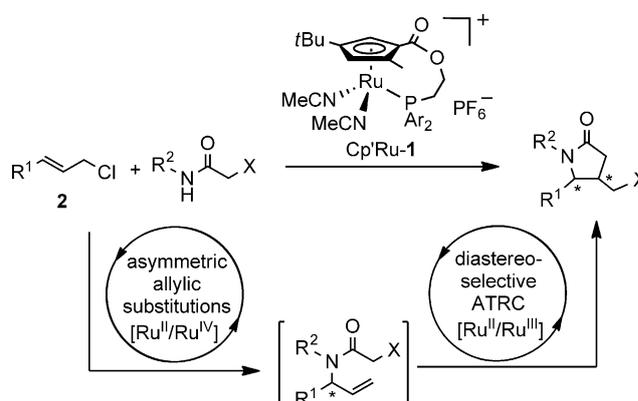
Naoya Kanbayashi, Kazuhiro Takenaka, Taka-aki Okamura,* and Kiyotaka Onitsuka*

The efficient synthesis of complex molecules with multiple stereogenic centers is a challenging task in synthetic organic chemistry. One-pot reactions have received considerable attention for the improvement of reaction efficiency, because they can avoid time-consuming workups and the often formidable isolation of intermediary products.^[1] A representative example is domino catalysis, in which two or more mechanistically similar reactions proceed in only one operation.^[1,2] Another method, auto-tandem catalysis is also an ideal and eco-friendly synthetic process, which involves two or more mechanistically distinct reactions promoted by only a single catalyst.^[3] Despite numerous examples of domino catalysis, there are limited numbers of reports on auto-tandem catalysis,^[4] this is probably due to the difficulty of optimizing the reaction conditions.

We have shown that planar-chiral cyclopentadienyl-ruthenium (Cp^{*}Ru) complex **1** is a proficient catalyst for asymmetric allylic substitutions.^[5,6] Recently, we succeeded in the development of regio- and enantioselective reactions of monosubstituted allylic halides with oxygen nucleophiles, which produced enantiomerically enriched branched allylic ethers, esters, and alcohols in good yields.^[7] These products possess a reactive terminal olefin, which can be potentially applied in a further transformation.^[7d,8] As the catalytic activity of **1** is preserved, even at the end of the allylic substitution,^[7b] and ruthenium complexes show various desirable oxidation states for catalytic behavior,^[9] we conceived an extension of our system to auto-tandem asymmetric catalysis. As a candidate for the transformation of a terminal olefin on a branched allylic compound, we focused on the atom-transfer radical cyclization (ATRC) because half-sandwiched Ru complexes similar to **1** are known to promote this

reaction.^[10] ATRC is an atom-economical method for the formation of cyclic compounds, which proceeds under mild conditions and exhibits broad functional group tolerance. Hence, it was hypothesized that complex **1** could realize an asymmetric auto-tandem catalysis consisting of allylic substitution and ATRC.

To test this theory, we envisioned the facile synthesis of optically active γ -lactams, an important structural motif found in a variety of biologically active molecules.^[11] Nagashima and co-workers reported that ATRC reaction of branched allylic amides using a Ru catalyst proceeded diastereoselectively,^[12,13] with the configuration at the new stereogenic carbon controlled by the stereochemistry of the substrate. The preparation of optically active allylic amides by **1**-catalyzed enantioselective allylic amidation would therefore provide γ -lactams with multiple stereogenic centers in a pure form through **1**-catalyzed ATRC (Scheme 1). Herein, we report



Scheme 1. Synthesis of enantiomerically enriched γ -lactams through auto-tandem asymmetric catalysis using **1**.

a sequential regio-, enantio-, and diastereoselective reaction of allylic chlorides with amide derivatives promoted by a single catalyst, **1**, and involving completely different reaction mechanisms. To the best of our knowledge, this is a novel example of asymmetric auto-tandem catalysis.

To accomplish the asymmetric auto-tandem catalysis, we initially examined the enantioselective allylic amidation^[13–15] of cinnamyl chloride (**2a**) using (*S*)-**1** (Ar = 3,5-Me₂C₆H₃) as the catalyst. After optimization of the conditions in the reaction of trifluoroacetamide (**3a**), we observed the formation of desired branched allylic amide **4a** with high regio- and enantioselectivity. Thus, treatment of **2a** and **3a** with (*S*)-**1** (1 mol%) in the presence of K₂CO₃ and 3 Å molecular

[*] N. Kanbayashi, Dr. T. Okamura, Prof. K. Onitsuka
 Department of Macromolecular Science
 Graduate School of Science, Osaka University
 Machikaneyama 1-1, Toyonaka
 Osaka 560-0043 (Japan)
 E-mail: tokamura@chem.sci.osaka-u.ac.jp
 onitsuka@chem.sci.osaka-u.ac.jp

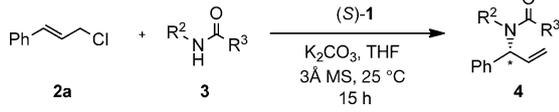
Dr. K. Takenaka

The Institute of Scientific and Industrial Research (ISIR)
 Osaka University, Mihogaoka, Ibaraki, Osaka 567-0047 (Japan)

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Table 1: Reaction of allylic chlorides **2** with amide **3**.^[a]



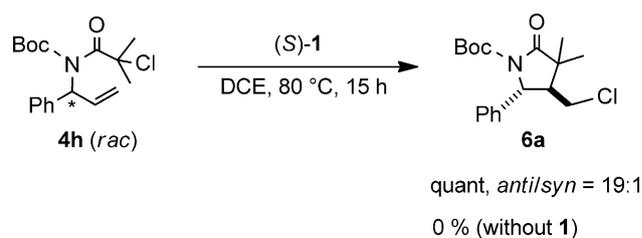
Entry	3	Yield [%] ^[b,c]	<i>ee</i> [%] ^[d]
1	 (3a)	80 (4a)	98 (<i>R</i>) ^[f]
2	 (3b)	0 (4b)	–
3	 (3c)	99 (4c)	96
4	 (3d)	90 (4d)	96
5	 (3e)	99 (4e)	96
6 ^[e]	 (3f)	99 (4f)	95 (<i>R</i>) ^[f]
7	 (3g)	99 (4g)	96 (<i>R</i>) ^[f]
8	 (3h)	96 (4h)	98

[a] Reaction conditions: (S)-**1** (5 μmol), **2** (0.60 mmol), **3** (0.50 mmol), K₂CO₃ (0.6 mmol), THF (2.0 mL), 25 °C, 15 h. [b] Yield of isolated product. [c] In each case, the branched product was selectively formed (branched/linear > 20:1). [d] Determined by HPLC analysis on a chiral stationary phase. [e] KHCO₃ was used instead of K₂CO₃. [f] Absolute configuration determined by comparison of the specific rotation with literature values.

sieves (3 Å MS) at 25 °C in THF afforded **4a** in 80 % yield with 98 % *ee* (Table 1, entry 1). However, benzamide (**3b**) did not react at all under otherwise identical conditions (entry 2). These observations implied the crucial role of the acidity of the amide NH group in this catalysis. Amides **3c–f**, protected with *tert*-butoxycarbonyl (Boc), carboxybenzyl (Cbz), trimethylsilylethoxycarbonyl (Teoc), or benzyloxy (BnO) groups, could be used as nucleophiles to produce the corresponding allylic amides **4c–f** in excellent yields with high enantioselectivities (entries 3–6). Moreover, reaction with phthalimide (**3g**), which is known as an ammonia equivalent, also proceeded smoothly to give **4g** quantitatively (entry 7). The substrate α -chloroamide (**3h**) was also applicable to this reaction without any loss in yield or enantioselectivity; amide **4h**, which bears a terminal olefin and chloroalkyl group, was obtained in 96 % yield with 98 % *ee* (entry 8).

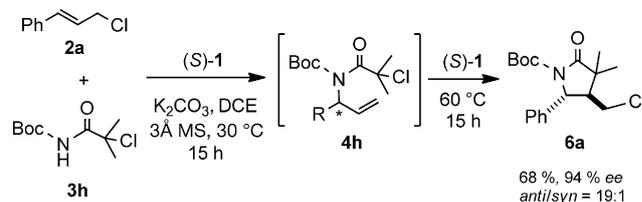
To realize asymmetric auto-tandem catalysis, we next investigated the catalytic activity of **1** in ATRC. When racemic **4h** was heated at 80 °C in 1,2-dichloroethane (DCE) with **1** (1 mol %) for 15 h, ATRC took place to give γ -lactam **6a** diastereoselectively and in quantitative yield (Scheme 2). No reaction was observed without the use of **1**, which strongly indicates that complex **1** indeed worked as a catalyst in this ATRC.

As Cp*Ru complex **1** turned out to be an effective catalyst in both the allylic amidation and ATRC, we applied it in the asymmetric auto-tandem catalysis. To our delight, when the



Scheme 2. Atom-transfer radical cyclization catalyzed by Cp*Ru complex **1**.

reaction mixture was warmed to 60 °C after the asymmetric allylic amidation reaction of **2a** with α -chloroamide **3h**, the ATRC reaction proceeded successively. The target γ -lactam **6a** was obtained in 68 % yield with 94 % *ee* and 19:1 d.r., with the *anti* diastereomer predominantly formed (Scheme 3).



Scheme 3. Asymmetric auto-tandem catalysis.

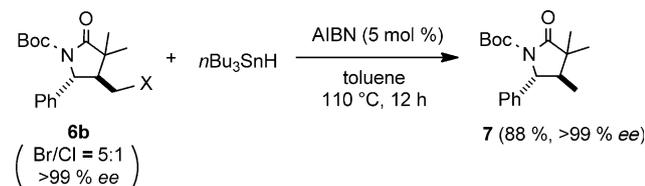
Subsequently, we examined a more reactive substrate for ATRC, α -bromoamide **5**, in an effort to simplify this auto-tandem catalysis. The auto-tandem reaction of **2a** with α -bromoamide **5a** was found to take place at 30 °C, leading to the diastereo- and enantioselective formation of γ -lactam **6b** (*anti/syn* = 19:1, *anti* isomer formed with 92 % *ee*) along with ca. 20 % of the chloride analogue **6a** in 99 % combined yield (Table 2, entry 1).^[16] Upon recrystallization, the diastereo- and enantiopurities of product **6b** were improved to > 20/1 d.r. and > 99 % *ee*. The substrate scope of this auto-tandem reaction is summarized in Table 2. In each case, the desired γ -lactam was obtained quantitatively as an inseparable mixture of the bromide and the chloride forms, and with high diastereo- and enantioselectivities. The α -bromoamide substrate **5b**, which bears a Cbz protecting group, produced optically active γ -lactam **6c**, whose absolute configuration was unequivocally determined to be (*R,R*) by X-ray crystallographic analysis of an enantiomerically pure sample.^[17] Various allylic chlorides were applicable to the auto-tandem catalysis, aryl-substituted γ -lactams **6d–f**, as well as alkyl-substituted **6g** were obtained with high diastereo- and enantioselectivities (entries 3–6).

Although a small amount of the chloride analogue accompanied the major product in this reaction, the mixture was easily transformed into a sole product (**7**) through a reductive dehalogenation reaction. The treatment of optically pure γ -lactam **6b**, whether Br or Cl atoms were present on the side chain, with *n*Bu₃SnH and a catalytic amount of 2,2'-azobis(isobutyronitrile) (AIBN) in toluene at 110 °C resulted in the formation of **7** in 88 % yield without racemization (Scheme 4).

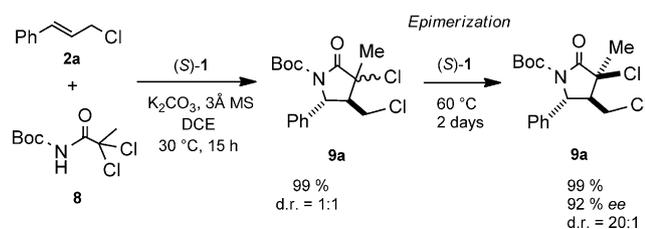
Table 2: Reaction of allylic chlorides **2** with amide **5**.^[a]

Entry	R ¹	R ²	Yield [%] ^[b]	anti/syn ^[c]	Br/Cl ^[d,e]	ee [%] ^[f]
1	Ph	(2a) (5a)	99 (85)	19:1 (>20:1)	5:1	92 (>99)
2	Ph	(2a) (5b)	99 (93)	19:1 (>20:1)	10:1	93 (>99) (R,R) ^[g]
3		(2b) (5a)	99 (75)	20:1 (>20:1)	5:1	92 (96)
4		(2c) (5a)	94 (68)	20:1 (>20:1)	10:1	94 (96)
5		(2d) (5a)	99 (67)	11:1 (>20:1)	10:1	89 (>99)
6		(2e) (5b)	99 (67) ^[h]	10:1 (>20:1)	> 20:1	91

[a] Reaction conditions: (S)-**1** (5 μmol), **2** (0.60 mmol), **5** (0.50 mmol), K₂CO₃ (0.60 mmol), CH₂Cl₂ (2.0 mL), 30 °C, 15 h. [b] Determined by ¹H NMR spectroscopy, the combined yield of isolated Br and Cl species is given in parentheses. [c] Determined by ¹H NMR spectroscopy of the crude product. The d.r. of isolated products is shown in parentheses. [d] Br: X = Br, Cl: X = Cl. [e] Determined by ¹H NMR spectroscopy. [f] Determined by HPLC analysis on a chiral stationary phase. The ee of isolated products is shown in parentheses. [g] Absolute configuration determined by X-ray crystallographic analysis.


Scheme 4. Reductive dehalogenation of **6b**. Br/Cl refers to the ratio of products where X = Br or Cl.

Finally, we examined the reactivity of α -dichloroamide **8** in this asymmetric auto-tandem catalysis, which would produce a γ -lactam with three consecutive stereogenic centers. When the reaction of **8** with **2a** was carried out under conditions similar to those in Table 2, the desired γ -lactam **9a** was obtained quantitatively (Scheme 5). The diastereomeric ratio at the carbon atom adjacent to the carbonyl group, however, was as low as 1:1. We were pleased


Scheme 5. Control of three stereogenic centers in tandem catalysis. Yields shown were determined by ¹H NMR spectroscopy.

to find that the epimerization of **9a** occurred at a slightly higher temperature in the presence of **1** to afford the thermodynamically stable diastereomer.^[18] Thus, heating of the reaction mixture at 60 °C for 2 days after the auto-tandem catalysis increased the diastereomeric ratio to 20:1. X-ray crystallographic analysis of enantio- and diastereopure **9c** established its relative and absolute configurations.^[17] With the favorable conditions for the production of γ -lactam **9** in hand, we conducted the reaction of several cinnamyl chloride derivatives with **8** (Table 3). Although the diastereoselectivity was not so high even after the epimerization, recrystallization of the products furnished γ -lactam **9b–d** with excellent diastereo- and enantiopurities.

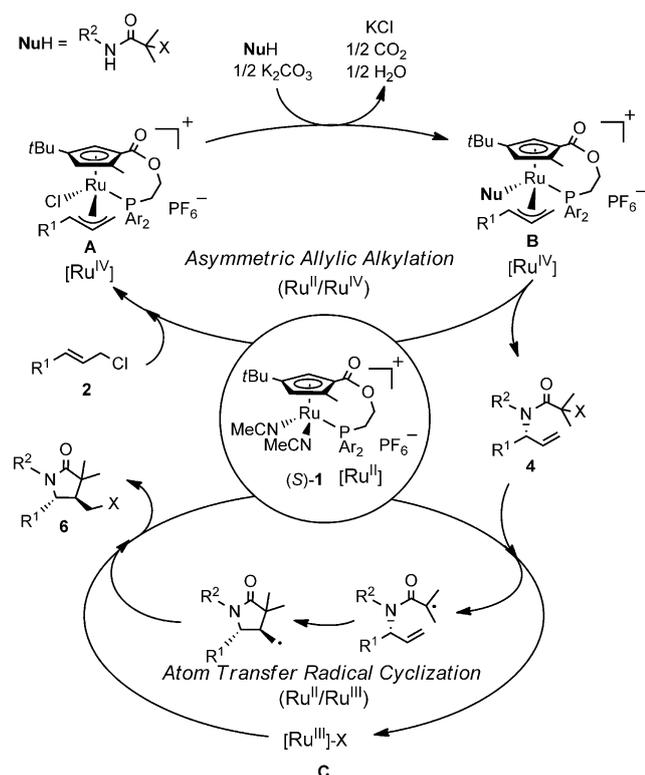
Table 3: Reaction of allylic chlorides **2** with amides **8**.^[a]

Entry	R ¹	Yield [%] ^[b]	d.r. ^[c]	ee [%] ^[d]
1	Ph	99 (9a) (68)	20:1 (>20:1)	92 (99)
2		99 (9b) (54)	6:1 (>20:1)	– ^[e] (92)
3		94 (9c) (53)	6:1 (>20:1)	92 (>99) (R,R) ^[f]
4		99 (9d) (66)	4:1 (>20:1)	91 (>99)

[a] Reaction conditions: (S)-**1** (5 μmol), **2** (0.50 mmol), K₂CO₃ (0.60 mmol), 1,2-dichloroethane (2.0 mL), 30 °C, 15 h. [b] Determined by ¹H NMR spectroscopy, yield of isolated products is given in parentheses. [c] Diastereomeric ratio at the 3 position determined by ¹H NMR spectroscopy of the crude product. The d.r. of isolated products is shown in parentheses. [d] Determined by HPLC analysis on a chiral stationary phase. The ee of isolated products is shown in parentheses. [e] Not determined. [f] Absolute configuration determined by X-ray crystallographic analysis.

A proposed reaction mechanism is shown in Scheme 6. Oxidative addition of **2** to (S)-**1** forms key π -allylic intermediate **A**,^[7] and triggers this auto-tandem asymmetric catalysis. Subsequent “inside” attack of the amidate by Ru amidate complex **B** gives the initial product, branched allyl amide **4**.^[7] The high enantioselectivity and the absolute configuration of the final product can be determined at the allylic amidation stage. The atom transfer reaction between (S)-**1** and **4** then furnishes [Ru^{III}]-X intermediate **C** and a tertiary radical species, of which the latter reacts with the terminal olefin in an intramolecular fashion. Finally, the X atom on [Ru^{III}] complex **C** recombines with the resulting primary radical to yield γ -lactam **6**.

In conclusion, we have developed an asymmetric auto-tandem allylic amidation/ATRC reaction, which proceeds in a highly regio-, diastereo-, and enantioselective manner, catalyzed solely by planar-chiral Cp*/Ru complex **1**. Optically active γ -lactams are constructed from readily available substrates in one pot. A characteristic redox property of ruthenium complexes may work expediently in different types



Scheme 6. Proposed reaction mechanism of asymmetric auto-tandem catalysis.

of catalyses involving mechanistically distinct allylic substitutions ($\text{Ru}^{\text{II}}/\text{Ru}^{\text{IV}}$) and atom-transfer radical cyclizations ($\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$), thus leading to the present asymmetric auto-tandem reaction. The results demonstrate that asymmetric auto-tandem catalysis is an atom-economical and environmentally benign synthetic method for producing useful chiral compounds. Further development of the auto-tandem reaction using other asymmetric allylic substitutions promoted by catalyst **1** is now in progress.

Experimental Section

General procedure: A solution of allylic chloride (0.50 mmol) in THF (2.0 mL) was added to a mixture of K_2CO_3 (0.60 mmol), (*S*)-**1** (5 μmol , 1 mol %), amide (0.60 mmol), and 3 Å MS, and then stirred for 15 h at 30 °C. After dilution with diethyl ether, the reaction mixture was filtered through Celite and the filtrate was concentrated under reduce pressure. The residue was purified by silica gel column chromatography (using a solvent gradient from toluene up to 7:3 Hex/EtOAc) followed by recrystallization from *n*-hexane to give a colorless crystal.

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[1] For reviews, see: a) L. F. Tietze, U. Beifuss, *Angew. Chem.* **1993**, *105*, 137–170; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 131–163;

b) L. F. Tietze, *Chem. Rev.* **1996**, *96*, 115–136; c) L. F. Tietze, G. Brasche, K. M. Gericke in *Domino Reactions in Organic Synthesis*, Wiley-VCH, Weinheim, **2006**; d) K. C. Nicolaou, D. J. Edmonds, P. Bulger, *Angew. Chem.* **2006**, *118*, 7292–7344; *Angew. Chem. Int. Ed.* **2006**, *45*, 7134–7186; e) H. Pellissier, *Adv. Synth. Catal.* **2012**, *354*, 237–294.

[2] In this manuscript, the reactions below are classified as domino reactions, because the catalyst conducts two or more mechanistically similar reactions: a) D. Enders, M. Hüttl, C. Grondal, G. Raabe, *Nature* **2006**, *441*, 861–863; b) H. Guo, J. Ma, *Angew. Chem.* **2006**, *118*, 362–375; *Angew. Chem. Int. Ed.* **2006**, *45*, 354–366; c) S. E. Denmark, A. Thorarensen, *Chem. Rev.* **1996**, *96*, 137–165.

[3] The term “Tandem catalysis” was defined by Fogg and Santos. In this manuscript, we follow their classification. For reviews on tandem catalysis, see: a) D. E. Fogg, E. N. dos Santos, *Coord. Chem. Rev.* **2004**, *248*, 2365–2379; b) A. Ajamian, J. L. Gleason, *Angew. Chem.* **2004**, *116*, 3842–3848; *Angew. Chem. Int. Ed.* **2004**, *43*, 3754–3760; c) J.-C. Wasilke, S. J. Obrey, R. T. Baker, G. C. Bazan, *Chem. Rev.* **2005**, *105*, 1001–1020; d) N. Shindoh, Y. Takemoto, K. Takasu, *Chem. Eur. J.* **2009**, *15*, 12168–12179; e) J. Zhou, *Chem. Asian J.* **2010**, *5*, 422–434.

[4] For selected examples of auto-tandem catalysis, see: a) P. A. Evans, J. E. Robinson, *J. Am. Chem. Soc.* **2001**, *123*, 4609–4610; b) B. A. Seigal, C. Fajardo, M. L. Snapper, *J. Am. Chem. Soc.* **2005**, *127*, 16329–16332; c) S. Fustero, D. Jiménez, M. Sánchez-Rosellò, C. del Pozo, *J. Am. Chem. Soc.* **2007**, *129*, 6700–6701; d) J.-R. Chen, C.-F. Li, X.-L. An, J.-J. Zhang, X.-Y. Zhu, W.-J. Xiao, *Angew. Chem.* **2008**, *120*, 2523–2526; *Angew. Chem. Int. Ed.* **2008**, *47*, 2489–2492.

[5] a) N. Dodo, Y. Matsushima, M. Uno, K. Onitsuka, S. Takahashi, *J. Chem. Soc. Dalton Trans.* **2000**, 35–41; b) Y. Matsushima, N. Komatsuzaki, Y. Ajioka, M. Yamamoto, H. Kikuchi, Y. Takata, N. Dodo, K. Onitsuka, M. Uno, S. Takahashi, *Bull. Chem. Soc. Jpn.* **2001**, *74*, 527–537.

[6] a) Y. Matsushima, K. Onitsuka, T. Kondo, T. Mitsudo, S. Takahashi, *J. Am. Chem. Soc.* **2001**, *123*, 10405–10406; b) K. Onitsuka, Y. Matsushima, S. Takahashi, *Organometallics* **2005**, *24*, 6472–6474.

[7] a) K. Onitsuka, H. Okuda, H. Sasai, *Angew. Chem.* **2008**, *120*, 1476–1479; *Angew. Chem. Int. Ed.* **2008**, *47*, 1454–1457; b) N. Kanbayashi, K. Onitsuka, *J. Am. Chem. Soc.* **2010**, *132*, 1206–1207; c) N. Kanbayashi, K. Onitsuka, *Angew. Chem.* **2011**, *123*, 5303–5305; *Angew. Chem. Int. Ed.* **2011**, *50*, 5197–5199; d) K. Takii, N. Kanbayashi, K. Onitsuka, *Chem. Commun.* **2012**, *48*, 3872–3874.

[8] a) A. Alexakis, C. Croset, *Org. Lett.* **2002**, *4*, 4147–4149; b) A. W. van Zijl, W. Szymanski, F. López, A. J. Minnaard, B. L. Feringa, *J. Org. Chem.* **2008**, *73*, 6994–7002; c) L. M. Stanley, J. F. Hartwig, *J. Am. Chem. Soc.* **2009**, *131*, 8971–8983; d) A. Farwick, J. U. Engelhart, O. Tverskoy, C. Welter, Q. A. Umlauf (née Stang), F. Rominger, W. J. Kerr, G. Helmchen, *Adv. Synth. Catal.* **2011**, *353*, 349; e) M. Gärtner, R. Weihofen, G. Helmchen, *Chem. Eur. J.* **2011**, *17*, 7605–7622.

[9] a) T. Naota, H. Takaya, S. Murahashi, *Chem. Rev.* **1998**, *98*, 2599–2660; b) B. M. Trost, F. D. Toste, A. B. Pinkerton, *Chem. Rev.* **2001**, *101*, 2067–2096.

[10] a) F. Simal, L. Wlodarczak, A. Demonceau, A. F. Noels, *Tetrahedron Lett.* **2000**, *41*, 6071–6074; b) F. Simal, L. Wlodarczak, A. Demonceau, A. F. Noels, *Eur. J. Org. Chem.* **2001**, 2689–2695; c) H. Nagashima, M. Gondo, S. Masuda, H. Kondo, Y. Yamaguchi, K. Matsubara, *Chem. Commun.* **2003**, 442–443; d) Y. Motoyama, M. Gondo, S. Masuda, Y. Iwashita, H. Nagashima, *Chem. Lett.* **2004**, *33*, 442–443; e) K. Thommes, B. Içli, R. Scopellitti, K. Severin, *Chem. Eur. J.* **2007**, *13*, 6899–6907.

- [11] a) A. I. Meyers, I. Snyder, *J. Org. Chem.* **1993**, *58*, 36–42; b) A. G. M. Barrett, J. Head, M. L. Smith, N. S. Stock, *J. Org. Chem.* **1999**, *64*, 6005–6018; c) C. Milne, A. Powell, J. Jim, M. I. Nakeeb, C. P. Smith, J. Micklefield, *J. Am. Chem. Soc.* **2006**, *128*, 11250–11259; d) X. Zhao, D. DiRocco, A. T. Rovis, *J. Am. Chem. Soc.* **2011**, *133*, 12466–12469.
- [12] a) H. Nagashima, H. Wakamatsu, N. Ozaki, T. Ishii, M. Watanabe, T. Tajima, K. Itoh, *J. Org. Chem.* **1992**, *57*, 1682–1689; b) H. Nagashima, N. Ozaki, M. Ishii, K. Seki, M. Washiyama, K. Itoh, *J. Org. Chem.* **1993**, *58*, 464–470; c) S. Iwamatsu, K. Matsubara, H. Nagashima, *J. Org. Chem.* **1999**, *64*, 9625–9631; d) M. A. Rachita, G. A. Slough, *Tetrahedron Lett.* **1993**, *34*, 6821–6824.
- [13] a) H. Miyabe, A. Matsumura, K. Moriyama, Y. Takemoto, *Org. Lett.* **2004**, *6*, 4631–4634; b) M. Gärtner, M. Jäkel, M. Achaiz, C. Sonnenschein, O. Tverskoy, G. Helmchen, *Org. Lett.* **2011**, *13*, 2810–2813.
- [14] a) O. M. Singh, H. Han, *J. Am. Chem. Soc.* **2007**, *129*, 774–775; b) O. M. Singh, H. Han, *Org. Lett.* **2007**, *9*, 4801–4804.
- [15] a) R. Weihofen, O. Tverskoy, G. Helmchen, *Angew. Chem.* **2006**, *118*, 5673–5676; *Angew. Chem. Int. Ed.* **2006**, *45*, 5546–5549; b) M. J. Pouy, A. Leitner, D. J. Weix, S. Ueno, J. F. Hartwig, *Org. Lett.* **2007**, *9*, 3949–3952; c) J. F. Teichert, M. Fañanàs-Mastral, B. L. Feringa, *Angew. Chem.* **2011**, *123*, 714–717; *Angew. Chem. Int. Ed.* **2011**, *50*, 688–691.
- [16] This result was confirmed by ¹H NMR and mass spectrometry, see the Supporting Information.
- [17] Summary of crystal data for **6c** and **9c** is given in the Supporting Information. CCDC 919708 (**6c**) and 919709 (**9c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
- [18] M. Benedetti, L. Forti, F. Ghelfi, U. M. Pagnoni, R. Ronzoni, *Tetrahedron* **1997**, *53*, 14031–14042.