

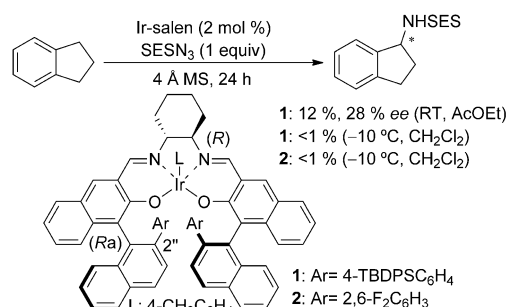
Enantio- and Regioselective Intermolecular Benzylic and Allylic C–H Bond Amination**

Yota Nishioka, Tatsuya Uchida, and Tsutomu Katsuki*

C–N bonds appear in the frameworks of various natural products, and their stereoselective formation is an important objective in organic synthesis. With the benefit of asymmetric nitrene-transfer catalysis by transition metal complexes,^[1] remarkable advancements have been made in stereoselective C–N bond formation, and many highly enantioselective methods have been reported.^[2–4] However, these reactions use low-atom-efficient nitrene precursors such as *N*-tosyliminophenylidene or in situ prepared equivalents. Thus, C–H amination using atom-efficient azides, especially ones bearing a readily removable *N*-protecting group, as nitrene precursors have attracted a growing interest.^[5] Although efficient methods for C–H amination using azides have been recently reported, they are not enantioselective,^[6–8] and enantiocontrol in C–H amination using an azide is still a great challenge.

We recently found that intramolecular benzylic C–H amination could be implemented with high enantioselectivity using iridium–salen complex **1** as the catalyst,^[9] and further explored an intermolecular version of C–H amination with complex **1** at room temperature. However, the amination of indane was slow and the enantioselectivity was poor (Scheme 1).

Previously, we discovered that Ru(CO)–salen complexes (**3–5**, Figure 1), especially durable ones (**4** and **5**) bearing



Scheme 1. Benzylic C–H amination of indane with iridium–salen complexes as catalysts. TBDPS = *tert*-butyldiphenylsilyl.

a 3,5-dihalo-substituted phenyl group at C2'', were good catalysts for asymmetric aziridination with azides as nitrene precursors.^[10] During the study, we observed that the reactions of some conjugated olefins with complex **3** gave allylic C–H amination products, albeit with moderate enantioselectivity and low yields.^[10c] Taking this observation as a clue, we investigated the asymmetric catalysis of C–H amination by a Ru(CO)–salen complex. Herein, we report highly enantio- and regioselective benzylic and allylic C–H amination.

We first examined benzylic C–H amination of indane using a series of (*Ra,R*)-Ru(CO)–salen complexes, which have cyclohexanediamine as the diamine subunit, as catalysts in the presence of 2-(trimethylsilyl)ethanesulfonyl azide^[11,12] (SES azide; caution: this compound is potentially explosive and must be handled in a fume hood.)^[13] and 4 Å molecular sieves (MS) at –10 °C in 1,1,2,2-tetrachloroethane. Complex **3** was found to catalyze C–H amination with high enantioselectivity, but low yield (Table 1, entry 1). The reaction with the robust complex **5**, which bears a 3,5-dichloro-4-trimethylsilylphenyl group at C2''^[10a] gave better yield, but the enantioselectivity was moderate (entry 2). The C–H amination product was accompanied by a small or trace amount of a diamination product (Table 1, footnote [c]). The yield was improved by using complex **6**, which bears a 3,5-dichlorophenyl group; however, **6** showed somewhat lower enantioselectivity than **3** (entry 3). These results suggested that a complex bearing a less bulky and poorly oxidizable aryl group at C2'' might be an appropriate catalyst for C–H amination. Thus, we examined reactions with complexes **7–10**, which bear a robust and less bulky group at C2'' (entries 4–7).^[14] A high enantioselectivity of 95% *ee* and better yield were obtained when **8** was used as a catalyst (entry 5). Complex **9** was poorly active as a catalyst (entry 6) and complex **10**, the diastereomer of **8**, did not show catalytic activity (entry 7). We next examined the reaction with **8** at

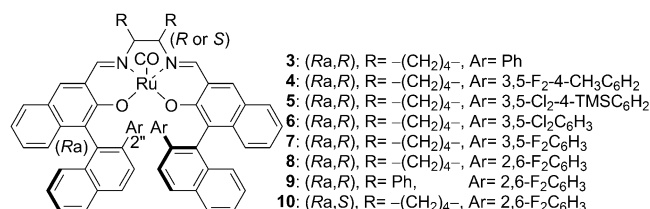


Figure 1. Ru(CO)–salen complexes. TMS = trimethylsilyl.

[*] Y. Nishioka, Dr. T. Uchida, Prof. T. Katsuki
Department of Chemistry, Faculty of Science, Graduate School, and International Institute for Carbon-Neutral Energy Research (WPI-I2CNER), Kyushu University, Hakozaki Higashi-ku, Fukuoka 812-8581 (Japan)
E-mail: katsuscc@chem.kyushu-univ.jp

[**] Financial support from Nissan Chemical Industries, Ltd., the World Premier International Research Center Initiative (WPI-I2CNER), the Global COE Programs, "Science for Future Molecular Systems", and Grants-in-Aid for Scientific Research (23245009) from MEXT (Japan) is gratefully acknowledged. We are also grateful to Hideki Kobayashi and Kenji Suzuki, of Nissan Chemical Industries, Ltd. for DSC measurement of SESN₃.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/ange.201208906>.

Table 1: Benzylic C–H amination of indane using Ru(CO)–salen complexes **3–10** as catalysts.^[a]

Entry	Cat.	Solvent	T [°C]	Yield [%] ^[b,c]	ee [%] ^[d]
1	3	(CHCl ₂) ₂	–10	4	85
2	5	(CHCl ₂) ₂	–10	33	56
3	6	(CHCl ₂) ₂	–10	44	83
4	7	(CHCl ₂) ₂	–10	42	92
5	8	(CHCl ₂) ₂	–10	51	95
6	9	(CHCl ₂) ₂	–10	trace	n.d.
7	10	(CHCl ₂) ₂	–10	n.r.	–
8	8	(CHCl ₂) ₂	25	24	91
9	8	CH ₂ Cl ₂	25	47	89
10 ^[e]	8	CH ₂ Cl ₂	25	5	65
11	8	CH ₂ Cl ₂	0	64	93
12	8	CH ₂ Cl ₂	–10	79	94
13	8	CH ₂ Cl ₂	–25	56	94
14 ^[f]	8	CH ₂ Cl ₂	–10	83	94
15 ^[f,g]	8	CH ₂ Cl ₂	–10	90 ^[h]	94

[a] Reactions were run with an indane/azide molar ratio of 1:1 at –10 °C with Ru catalyst (2 mol %), 4 Å MS (20 mg), and a 1.0 M substrate concentration on a 0.1 mmol scale under nitrogen, unless otherwise mentioned. [b] Yield of isolated product. [c] A trace amount of diamination product (monoamine/diamine > 20:1) was detected by ¹H NMR spectroscopy in all cases except for entries 1, 6, 7, and 10. Reaction with **5** gave the diamination product in 14% yield together with the major monoamination product. [d] Determined by HPLC analysis on a chiral stationary phase (DAICEL AD-3). [e] Run in the absence of 4 Å MS. [f] Run on a 0.3 mmol scale at 3.0 M substrate concentration. [g] Run with an indane/azide molar ratio of 1.3:1; the azide was completely consumed. [h] Yield is based on the amount of azide used. n.d. = not determined, n.r. = no reaction.

25 °C, but the yield and the enantioselectivity were both reduced, to 24% and 91% ee, respectively (entry 8). Under these conditions, we examined solvent effects for this reaction^[15] and found that dichloromethane gave a better yield (47%), albeit with slightly lower enantioselectivity (89% ee) (entry 9). Reaction in the absence of 4 Å MS gave the product in only 5% yield (entry 10). Thus, the reaction was examined at lower temperatures in dichloromethane in the presence of 4 Å MS (entries 11–13), and high enantioselectivity along with improved yield were obtained at –10 °C (entry 12). The reaction at a high substrate concentration (3.0 M) further improved the yield (entry 14), and the highest yield was obtained with a slight excess of indane (1.3 equiv) (entry 15). Under these optimized conditions, we reexamined the amination of indane with iridium–salen complexes **1** and **2**. However, the reaction with these catalysts gave less than 1% yield (Scheme 1).

Accordingly, C–H amination of various alkylarenes and alkenes was examined with **8** as the catalyst under the optimized conditions with 1.3 equivalents of alkylarene or alkene (Table 2). The reaction of ethylbenzene **11** in dichloromethane was highly enantioselective, but the yield was modest. However, an acceptable yield without deterioration of the enantioselectivity was obtained using **8** (4 mol %) in the presence of 5 Å MS^[16] under solvent-free conditions (entry 1). The reactions of other alkylarenes were also carried out under

Table 2: Benzylic and allylic C–H amination using Ru(CO)–salen complex **8** as a catalyst.^[a]

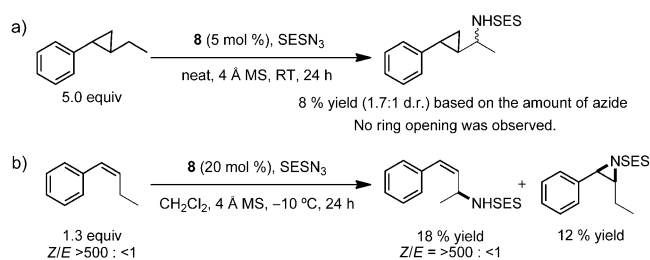
Entry	Substrate	t [h]	Yield [%] ^[b]	ee [%] ^[c]
1 ^[d]	Ph 11	4	77	96
2 ^[d]	MeO 12	2	97 (90) ^[e]	94 (93) ^[e]
3 ^[d]	Br 13	4	82	94
4 ^[d]	O ₂ N 14	6	75	97
5 ^[d]	MeO 15	3	73 ^[f]	87
6 ^[d]	16	2	99	93
7 ^[g,h]	17	24	79	96
8 ^[d]	Ph 18	24	n.r.	–
9 ^[d]	19	3	77	96
10 ^[e]	20	24	61	94
11 ^[e]	21	24	69	91
12 ^[i]	22	24	60	93
13 ^[d]	RO 23	10	81	91
14 ^[e]	R = TBDPS 24	24	99 (93) ^[j]	93
15 ^[d]	Ph 25	4	97	93
16 ^[e]	26	24	34 ^[k]	–
17 ^[e]	27	24	30 ^[l]	88
18 ^[e]	28	24	51	46
19 ^[e]	29	24	n.r.	–
20 ^[g,m]	20	24	n.r.	–
21 ^[d,h]	Ph 30	2	99	79
22 ^[e]	31	24	98	99

[a] The reactions were run at –10 °C with a substrate/azide molar ratio of 1.3:1, along with catalyst **8** (4 mol %) and 4 Å (or 5 Å) MS on a 0.3 mmol scale, unless otherwise mentioned. [b] Yield of isolated product based on the azide. [c] Determined by HPLC analysis on a chiral stationary phase (see the Supporting Information for details). [d] Run with 5 Å MS (20 mg) under solvent-free conditions. [e] The data in parentheses are the yield of isolated product and the enantioselectivity obtained from a 2 mmol scale reaction. [f] Yield of the *para*-isomer (*Meta*-isomer: 92% ee, 20% yield). [g] Run with CH₂Cl₂ (100 μL) and 4 Å MS (20 mg). [h] The reaction was run at 0 °C. [i] Run with CH₂Cl₂ (50 μL) and 4 Å MS (20 mg). [j] The number in the parentheses is the yield of the reaction with a 1:1 substrate/azide molar ratio. [k] C1 amination product. [l] Yield of the 4-aminated product; the yields of 1-aminated and 1,4-diaminated products were 21% and 3%, respectively. Yields were determined by ¹H NMR analysis of the crude mixture using phenanthrene as an internal standard. [m] Run in the presence of (*Z*)-3-heptene (1.3 equiv). n.r. = no reaction, TBDPS = *tert*-butyldiphenylsilyl.

solvent-free conditions. The reactions of 4-substituted ethylbenzenes **12**, **13**, and **14** proceeded with high enantioselectiv-

ity and good to high yield (entries 2–4). The reaction was also effective when carried out on a 2 mmol scale (data in parentheses, entry 2). The reaction of 5-methoxy-2,3-dihydro-1*H*-indene **15** occurred preferentially at the benzylic position *para* to the methoxy group with a high enantioselectivity (*para/meta* = 1.0:0.27; entry 5).^[17] The amination of 2,3-dihydrobenzofuran **16** and *N*-acetylindoline **17** occurred at the benzylic position with high enantioselectivity (entries 6 and 7). However, *n*-propylbenzene **18** did not undergo C–H amination (entry 8), whereas the amination of 1-ethyl-4-propylbenzene **19** was extremely regioselective and occurred only at the benzylic carbon of the ethyl group with the same enantioselectivity as that observed in the amination of ethylbenzene (entry 9). Complex **8** did not dissolve in alkene, and so the amination of (*E*)-3-hexene **20** was carried out in dichloromethane in the presence of 4 Å MS (20 mg) to give solely (*E*)-2-(*N*-SES-amino)-3-hexene with high enantioselectivity (entry 10). We next examined the reactions of (*E*)-3-alkenes **21**, **22**, and **23**, which have two different methylene carbons. The reactions were also extremely regioselective and occurred only at the ethyl group to give the corresponding (*E*)-2-(*N*-SES-amino)-3-alkenes as a single product with high enantioselectivity (entries 11–13). The (*E*)-disubstituted conjugated alkenes **24** and **25** also underwent highly enantioselective C–H amination (entries 14 and 15). Metal–nitrenoid species generally insert into methylene C–H bonds in preference to methyl C–H bonds.^[3a,7f,9] However, the amination of (*E*)-2-octene **26** occurred at C1, albeit slowly (entry 16). No C–H amination at C4 was observed. The reaction of (*E*)-2-pentene **27** gave a 10:7:1 mixture of 4-aminated/1-aminated/1,4-diaminated products in 54 % yield (entry 17). On the other hand, (*Z*)-alkenes are poor substrates for this amination. The reaction of cyclohexene **28** was slow and only modestly enantioselective (entry 18), whereas the reaction of (*Z*)-3-heptene **29** did not occur at all (entry 19). (*Z*)-3-Heptene **29** was more strongly coordinated to complex **8** than (*E*)-3-heptene **21**, and this coordination blocked the decomposition of SESN₃.^[18] Thus, the amination of **20** did not proceed in the presence of **29** (entry 20). However, the reactions of tri-substituted olefins proceeded with good to high enantioselectivity. 1-Phenylcyclohexene **30** underwent C–H amination to give 1-phenyl-3-(*N*-SES-amino)cyclohexene with 79 % *ee* (entry 21), and the reaction of 2-ethylindene **31** proceeded with high enantioselectivity (entry 22). No amination at C1 was observed.

There is controversy about whether C–H amination through a putative metal–nitrenoid intermediate proceeds in a concerted manner^[3a,19] or in a stepwise manner.^[20] To get insight into the mechanism, we examined the amination of *trans*-(2-ethylcyclopropyl)benzene, which is a radical clock (Scheme 2a).^[21] The reaction gave only two diastereomeric amination products, albeit in low yields. Neither the ring-opened product nor any other product was detected by ¹H NMR analysis.^[22] Recently, Du Bois et al.^[23a] and White et al.^[23b] independently proposed the intermediacy of a short-lived radical species in C–H amination through a putative metal–nitrenoid species, based on the isomerization of a *cis*-disubstituted cyclopropane^[23a] or a *Z*-substituted olefin substrate.^[23] Thus, to ascertain if this amination proceeds through



Scheme 2. Reactions of a radical clock and (*Z*)-1-phenyl-1-butene.

a short-lived radical, we examined the C–H amination of *cis*-2-ethyl-1-phenylcyclopropane and (*Z*)-1-phenyl-1-butene under the present conditions. *cis*-2-Ethyl-1-phenylcyclopropane did not react, but (*Z*)-1-phenyl-1-butene gave (*Z*)-3-(*N*-SES-amino)-1-phenyl-1-butene (18 % yield) together with an aziridine product (12 %; Scheme 2b). HPLC analysis of the amination product did not detect any (*E*)-3-(*N*-SES-amino)-1-phenyl-1-butene.^[22] This result supports a concerted mechanism for the present C–H amination; however, the intermediacy of a short-lived radical species cannot be completely ruled out, if the radical rebound is an extremely rapid step.

In summary, we have achieved a highly enantio- and regioselective intermolecular benzylic and allylic C–H bond amination using the new Ru(CO)–salen complex **8**, which bears a durable and less bulky 2,6-difluorophenyl group, as the catalyst and SES azide as the nitrene precursor. Under the present conditions, only ethyl, methyl, and cyclic methylene groups in the allylic or benzylic position can be aminated. It is noteworthy that an ethyl group can be selectively aminated in a highly enantioselective manner, even in the presence of an *n*-propyl group (Table 2, entries 9 and 11).

Experimental Section

Method A (Table 2, Entries 7, 10–12, 14, 16–20, and 22; reactions in CH₂Cl₂): The reaction was carried out in a Schlenk tube (5 mL) under N₂. Substrate (0.39 mmol), SES azide (0.3 mmol, 67.0 mg, 58.0 μL) and 4 Å MS (20 mg) were added in dry CH₂Cl₂ (the amount is given in the Table 2 footnotes) and stirred at –10 °C or 0 °C for 30 min. Subsequently, **8** (12.0 μmol, 12.3 mg, 4 mol %) was added, and the whole mixture was stirred for 24 h at –10 °C or 0 °C. The reaction mixture was filtered through a pad of Celite and concentrated. The residue was purified by silica gel chromatography (*n*-hexane/AcOEt = 20:1 to 4:1) to obtain an amination product.

Each reaction was repeated at least three times. One of the experiments was carried out in the presence of phenanthrene. An aliquot was taken after the reaction was complete and analyzed by ¹H NMR spectroscopy.

Method B (Table 2, Entries 1–6, 8, 9, 13, 15, and 21; under solvent free condition): The reaction was carried out in a Schlenk tube (5 mL) under N₂. Substrate (0.39 mmol), SES azide (0.3 mmol, 67.0 mg, 58.0 μL), and 5 Å MS (20 mg) were mixed and stirred at –10 °C or 0 °C for 30 min. Subsequently, **8** (12.0 μmol, 12.3 mg, 4 mol %) was added and the whole mixture was stirred at –10 °C or 0 °C. The mixture gradually became pasty and the stirrer stopped. After 1 h, the mixture was diluted with dichloromethane (100 μL). (For reaction time, see Table 2.) The mixture was filtered through a pad of Celite and concentrated on a rotatory evaporator. The residue was purified by silica gel chromatography (*n*-hexane/AcOEt = 20:1 to 4:1) to obtain an amination product. The product from Table 2, entry 5 was

further purified by silica gel chromatography (*n*-hexane/AcOEt/EtOH = 20:1:1).

Each reaction was repeated at least three times. One of the experiments was carried out in the presence of phenanthrene. One hour after the stirrer stopped, the mixture was diluted with CDCl₃ and analyzed by ¹H NMR spectroscopy.

Received: November 7, 2012

Published online: January 10, 2013

Keywords: asymmetric catalysis · azides · C–H amination · nitrenes · salen complexes

- [1] For reviews on metal-catalyzed C–H amination, see: a) H. Lu, X. P. Zhang, *Chem. Soc. Rev.* **2011**, *40*, 1899–1909; b) F. Collet, C. Lescot, P. Dauban, *Chem. Soc. Rev.* **2011**, *40*, 1926–1936; c) J. Du Bois, *Org. Process Res. Dev.* **2011**, *15*, 758–762; d) H. M. L. Davies, M. S. Long, *Angew. Chem.* **2005**, *117*, 3584–3586; *Angew. Chem. Int. Ed.* **2005**, *44*, 3518–3520; e) J. L. Roizen, M. E. Harvey, J. Du Bois, *Acc. Chem. Res.* **2012**, *45*, 911–922.
- [2] For selected papers of enantioselective C–H amination, see: a) D. N. Zalatan, J. Du Bois, *J. Am. Chem. Soc.* **2008**, *130*, 9220–9221; b) E. Milczek, N. Boudet, S. Blakey, *Angew. Chem.* **2008**, *120*, 6931–6934; *Angew. Chem. Int. Ed.* **2008**, *47*, 6825–6828; c) R. P. Reddy, H. M. L. Davies, *Org. Lett.* **2006**, *8*, 5013–5016; d) J.-L. Liang, S.-X. Yuan, J.-S. Huang, C.-M. Che, *J. Org. Chem.* **2004**, *69*, 3610–3619; e) J.-L. Liang, S.-X. Yuan, J.-S. Huang, W.-Y. Yu, C.-M. Che, *Angew. Chem.* **2002**, *114*, 3615–3618; *Angew. Chem. Int. Ed.* **2002**, *41*, 3465–3468; f) M. Yamawaki, H. Tsutsui, S. Kitagaki, M. Anada, S. Hashimoto, *Tetrahedron Lett.* **2002**, *43*, 9561–9564; g) Y. Kohmura, T. Katsuki, *Tetrahedron Lett.* **2001**, *42*, 3339–3342; h) I. Nägeli, C. Baud, G. Bernardinelli, Y. Jacquier, M. Moran, P. Müller, *Helv. Chim. Acta* **1997**, *80*, 1087–1105.
- [3] For asymmetric C–H amination using optically active sulfonimidamides as the nitrene precursors, see: a) C. Liang, F. Collet, F. Robert-Peillard, P. Müller, R. H. Dodd, P. Dauban, *J. Am. Chem. Soc.* **2008**, *130*, 343–350; b) C. Liang, F. Robert-Peillard, C. Fruit, P. Müller, R. H. Dodd, P. Dauban, *Angew. Chem.* **2006**, *118*, 4757–4760; *Angew. Chem. Int. Ed.* **2006**, *45*, 4641–4644; c) C. Lescot, B. Darses, F. Collet, P. Retailleau, P. Dauban, *J. Org. Chem.* **2012**, *77*, 7232–7240.
- [4] Shi and co-workers have reported Pd-catalyzed 3,4-diamination of terminal olefins using di-*tert*-butyldiaziridinone as a nitrogen source, which proceeds through a 1,3-diene intermediate; see: a) H. Du, W. Yuan, B. Zhao, Y. Shi, *J. Am. Chem. Soc.* **2007**, *129*, 7496–7497; for an asymmetric version, see: b) H. Du, B. Zhao, Y. Shi, *J. Am. Chem. Soc.* **2008**, *130*, 8590–8591; for another example of Pd-catalyzed C–H amination, see: c) H. Bao, U. K. Tambar, *J. Am. Chem. Soc.* **2012**, *134*, 18495–18498.
- [5] T. G. Driver, *Org. Biomol. Chem.* **2010**, *8*, 3831–3846.
- [6] a) F. Ragaini, A. Penoni, E. Gallo, S. Tollari, C. L. Gotti, M. Lapadula, E. Mangioni, S. Cenini, *Chem. Eur. J.* **2003**, *9*, 249–259; b) S. Cenini, E. Gallo, A. Penoni, F. Ragaini, S. Tollari, *Chem. Commun.* **2000**, 2265–2266; c) S. Cenini, S. Tollari, A. Penoni, C. Cereda, *J. Mol. Catal. A* **1999**, *137*, 135–146; d) D. Intrieri, M. Mariani, A. Caselli, F. Ragaini, E. Gallo, *Chem. Eur. J.* **2012**, *18*, 10487–10490; e) J. Y. Kim, S. H. Park, J. Ryu, S. H. Cho, S. H. Kim, S. Chang, *J. Am. Chem. Soc.* **2012**, *134*, 9110–9113; f) J. Ryu, K. Shin, S. H. Park, J. Y. Kim, S. Chang, *Angew. Chem.* **2012**, *124*, 10042–10046; *Angew. Chem. Int. Ed.* **2012**, *51*, 9904–9908.
- [7] a) H. Lu, H. Jiang, Y. Hu, L. Wojtas, X. P. Zhang, *Chem. Sci.* **2011**, *2*, 2361–2366; b) H. Lu, V. Subbarayan, J. Tao, X. P. Zhang, *Organometallics* **2010**, *29*, 389–393; c) H. Lu, H. Jiang, L. Wojtas, X. P. Zhang, *Angew. Chem.* **2010**, *122*, 10390–10394; *Angew. Chem. Int. Ed.* **2010**, *49*, 10192–10196; d) H. Lu, J. Tao, J. E. Jones, L. Wojtas, X. P. Zhang, *Org. Lett.* **2010**, *12*, 1248–1251; e) K. Sun, R. Sachwani, K. J. Richert, T. G. Driver, *Org. Lett.* **2009**, *11*, 3598–3601; f) Y. M. Badiei, A. Dinescu, X. Dai, R. M. Palomino, F. W. Heinemann, T. R. Cundari, T. H. Warren, *Angew. Chem.* **2008**, *120*, 10109–10112; *Angew. Chem. Int. Ed.* **2008**, *47*, 9961–9964; g) J. V. Ruppel, R. M. Kamble, X. P. Zhang, *Org. Lett.* **2007**, *9*, 4889–4892; h) A. L. Pumphrey, H. Dong, T. G. Driver, *Angew. Chem.* **2012**, *124*, 6022–6025; *Angew. Chem. Int. Ed.* **2012**, *51*, 5920–5923; i) H. Lu, Y. Hu, H. Jiang, L. Wojtas, X. P. Zhang, *Org. Lett.* **2012**, *14*, 5158–5161.
- [8] a) Y. Liu, J. Wei, C.-M. Che, *Chem. Commun.* **2010**, *46*, 6926–6928; b) Y. Liu, C.-M. Che, *Chem. Eur. J.* **2010**, *16*, 10494–10501; c) E. R. King, E. T. Hennessy, T. A. Betley, *J. Am. Chem. Soc.* **2011**, *133*, 4917–4923.
- [9] M. Ichinose, H. Suematsu, Y. Yasutomi, Y. Nishioka, T. Uchida, T. Katsuki, *Angew. Chem.* **2011**, *123*, 10058–10061; *Angew. Chem. Int. Ed.* **2011**, *50*, 9884–9887.
- [10] a) H. Kawabata, K. Omura, T. Uchida, T. Katsuki, *Chem. Asian J.* **2007**, *2*, 248–256; b) K. Omura, T. Uchida, R. Irie, T. Katsuki, *Chem. Commun.* **2004**, 2060–2061; c) K. Omura, M. Murakami, T. Uchida, R. Irie, T. Katsuki, *Chem. Lett.* **2003**, *32*, 354–355; d) T. Uchida, Y. Tamura, M. Ohba, T. Katsuki, *Tetrahedron Lett.* **2003**, *44*, 7965–7968.
- [11] For the SES protection of amino groups, see: S. M. Weinreb, D. M. Demko, T. A. Lessen, J. P. Demers, *Tetrahedron Lett.* **1986**, *27*, 2099–2102; for the synthesis of SESN₃, see the Supporting Information.
- [12] For the selection of the azide, see the Supporting Information, Table S1.
- [13] For measurement of differential scanning calorimetry, see the Supporting Information.
- [14] For the synthesis of complex **8**, see the Supporting Information.
- [15] For the solvent effect on yield and enantioselectivity, see the Supporting Information, Table S2.
- [16] Under solvent-free conditions, 5 Å MS was a better additive than 4 Å MS. Under solvent-free conditions, the reaction mixture became pasty and the stirrer stopped when the reaction came to an end. For the work-up procedure, see the Supporting Information.
- [17] Determined by ¹H NMR analysis.
- [18] For details, see the Supporting Information.
- [19] a) I. Nägeli, C. Baud, G. Bernardinelli, Y. Jacquier, M. Moran, P. Müller, *Helv. Chim. Acta* **1997**, *80*, 1087–1105; b) X. Lin, C. Zhao, C.-M. Che, Z. Ke, D. L. Phillips, *Chem. Asian J.* **2007**, *2*, 1101–1108.
- [20] a) S. K.-Y. Leung, W.-M. Tsui, J.-S. Huang, C.-M. Che, J.-L. Liang, N. Zhu, *J. Am. Chem. Soc.* **2005**, *127*, 16629–16640; b) J.-P. Mahy, G. Bedi, P. Battioni, D. Mansuy, *New J. Chem.* **1989**, *13*, 651–657; c) V. Lyaskovskyy, A. I. O. Suarez, H. Lu, H. Jiang, X. P. Zhang, B. de Bruin, *J. Am. Chem. Soc.* **2011**, *133*, 12264–12273.
- [21] a) K. Huard, H. Lebel, *Chem. Eur. J.* **2008**, *14*, 6222–6230; b) K. W. Fiori, J. Du Bois, *J. Am. Chem. Soc.* **2007**, *129*, 562–568; c) D. Griller, K. U. Ingold, *Acc. Chem. Res.* **1980**, *13*, 317–323; d) M. Newcomb, *Tetrahedron* **1993**, *49*, 1151–1176.
- [22] See the Supporting Information for details.
- [23] a) M. E. Harvey, D. G. Musaev, J. Du Bois, *J. Am. Chem. Soc.* **2011**, *133*, 17207–17216; b) S. M. Paradine, M. C. White, *J. Am. Chem. Soc.* **2012**, *134*, 2036–2039.