ChemComm
Chemical Communications

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: G. Liu, X. Zhang, H. Wang, H. Cong, X. Zhang and X. Dong, *Chem. Commun.*, 2020, DOI: 10.1039/D0CC01220C.

ROYAL SOCIETY OF CHEMISTRY

rsc.li/chemcomm

View Article Online
DOI: 10.1039/D0CC01220C

Journal Name

COMMUNICATION

Synthesis of Chiral α-Substituted α-Amino Acid and Amine Derivatives Through Ni-Catalyzed Asymmetric Hydrogenation

Gongyi Liu,[†] Xianghe Zhang,[†] Heng Wang,[§] Hengjiang Cong,[†] Xumu Zhang*[§,†] and Xiu-Qin Dong,*[†]

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

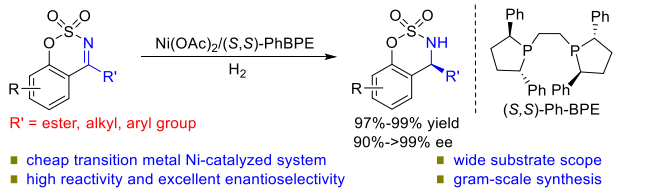
www.rsc.org/

Highly efficient Ni-catalyzed asymmetric hydrogenation of cyclic N-sulfonyl ketimino esters was first successfully developed, providing various chiral α-monosubstituted α-amino acid derivatives with excellent results (97%-99% yields, 90%->99% ee). The cyclic N-sulfonyl ketimines were also hydrogenated well to afford chiral amine derivatives with 98%-99% yields and 97%->99% ee. The gram-scale asymmetric hydrogenation was performed well with 85% yield and 99% ee using only 0.2 mol% catalyst. Interestingly, different nonlinear effects were observed with substrates cyclic N-sulfonyl ketimino ester 1a and ketimine 1m, which disclosed that there may be different nickel catalytic species in these reaction systems.

Chiral α-monosubstituted α-amino acid derivatives represent as an important class of nonproteinogenic amino acid derivatives, which are universally distributed in many pharmaceuticals and biologically active molecules.[1-6] In addition, they can be served as versatile chiral building blocks, auxiliaries, ligands in the field of asymmetric synthesis.[7-8] Owing to the enormous importance of chiral α-substituted α-amino acids and derivatives, they have attracted great attention in the last decades, and many asymmetric catalytic synthetic methodologies have been well established.[1c-1d, 9-15] However, most of them were focused on the synthesis of chiral α,α-disubstituted α-amino acid derivatives,[10-15] such as asymmetric addition of organic boronic reagents or terminal alkynes to ketimino esters,[10] allylation[12] and alkylation[13] of ketimino ester derivatives, addition of β-ketoesters or α-cyanoacetates to azodicarboxylate esters,[14] and 1,3-cycloaddition of azomethine ylides[15]. Comparatively, the asymmetric catalytic reaction types for the synthesis of chiral α-monosubstituted α-amino acid derivatives were relatively less explored, and it is necessary to develop new and efficient synthetic methods.

[a] *Key Laboratory of Biomedical Polymers, Engineering Research Center of Organosilicon Compounds & Materials, Ministry of Education, College of Chemistry and Molecular Sciences, Suzhou Institute of Wuhan University, Wuhan University, Wuhan, Hubei, 430072, P. R. China.*
[b] *Shenzhen Grubbs Institute, Department of Chemistry, Southern University of Science and Technology, Shenzhen, Guangdong, 518055, P. R. China.*
E-mail address: zhangxm@sustc.edu.cn, xiuqindong@whu.edu.cn.
‡ Electronic supplementary information (ESI) available: Experimental procedures, NMR spectra of compounds. See DOI: 10.1039/x0xx00000x.

Transition metal-catalyzed asymmetric hydrogenation of prochiral unsaturated compounds is a facile and direct method to access chiral compounds with the advantages of high atom economy and easy manipulation, which is heavily dependent on precious transition metals.[16] They could suffer from limited resource, high cost and environmental contamination. As an important strategy, the cheap and earth-abundant transition metal catalytic systems were paid increasing attention in recent years, which is helpful to the sustainable development. Some pioneering research works of Ni-catalyzed asymmetric hydrogenation of ketones, alkenes, ketimines and enamides have been reported by Hamada,[17] Chirik,[18] Zhou,[19] Zhang[20] and our group[21]. Zhang and coworkers successfully realized the highest catalytic activity for Ni-catalyzed asymmetric hydrogenation to date.[20a] Based on the long-standing study in this field, we are interested in developing efficient method to synthesize chiral α-monosubstituted α-amino acid derivatives through Ni-catalyzed asymmetric hydrogenation. The prochiral cyclic N-sulfonyl ketimines were proven as preferred substrates to construct chiral amine derivatives, because the -SO_2- group can be easily removed through simple transformation.[22] However, they are mainly restricted to aryl/alkyl substituted cyclic N-sulfonyl ketimines substrates, the cyclic N-sulfonyl ketimino esters were not investigated. Herein, we successfully realized the first Ni-catalyzed asymmetric hydrogenation of cyclic N-sulfonyl ketimino esters with excellent results, and the cyclic N-sulfonyl ketimines were also hydrogenated well to afford chiral amine derivatives (97%-99% yields, 90%->99% ee, Scheme 1).

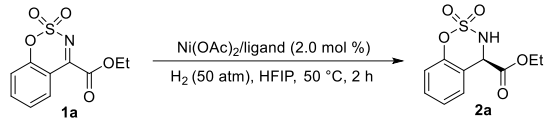


Scheme 1. Ni-catalyzed asymmetric hydrogenation of cyclic N-sulfonyl ketimino esters and ketimines.

Our preliminary investigation for the Ni-catalyzed asymmetric hydrogenation of cyclic N-sulfonyl ketimino ester was conducted with model substrate ethyl benzo[e][1,2,3]oxathiazine-4-carboxylate 2,2-dioxide **1a** under 50 atm H_2 in hexafluoroisopropanol (HFIP). As shown

in Table 1, a variety of chiral diphosphine ligands were applied. Full conversion and moderate enantioselectivity was provided with (*Rc*,*Sp*)-DuanPhos as the ligand (>99% conversion, 64% ee, Table 1, entry 1). Poor reactivities and enantioselectivities were observed in the presence of (*S*)-Binapine, (*S*,*S*)-Me-DuPhos (6%-13% conversions, 30% ee, Table 1, entries 2, 5). There was trace conversion or no reaction using ligands (*S*)-BINAP, ZhaoPhos, (*S*)-SegPhos and WalPhos (Table 1, entries 4, 6-8). To our delight, the (*S*,*S*)-Ph-BPE gave full conversion and 96% ee (Table 1, entry 3).

Table 1. Screening ligands for Ni-catalyzed asymmetric hydrogenation of **1a**. [a]



Entry	Ligand	Conv. (%)[b]	Ee (%)[c]
1	(*Rc*,*Sp*)-DuanPhos	>99	64
2	(*S*)-Binapine	13	30
3	(*S*,*S*)-Ph-BPE	>99	96
4	(*S*)-BINAP	trace	70
5	(*S*,*S*)-Me-DuPhos	6	30
6	ZhaoPhos	NR	NA
7	(*S*)-SegPhos	trace	33
8	WalPhos	NR	NA

[a] Unless otherwise noted, all reactions were carried out with a $Ni(OAc)_2$/ligand/**1a** (0.05 mmol) ratio of 1:1.1:50 at 50 °C in 0.7 mL HFIP under 50 atm H_2 for 2 h. [b] Determined by ^1H NMR analysis. [c] Determined by HPLC on a chiral phase. NR = No Reation, NA = Not Available.

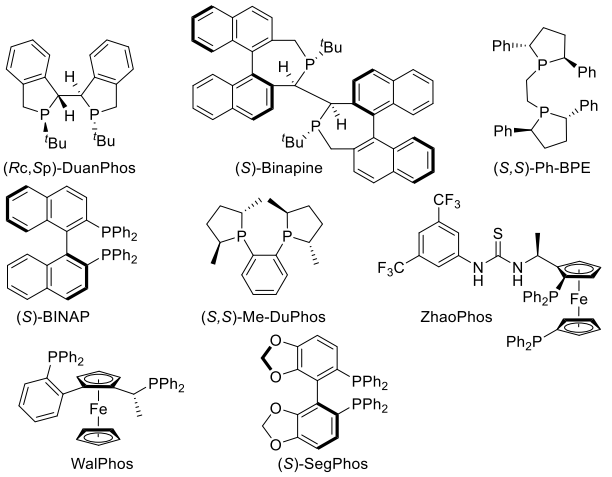
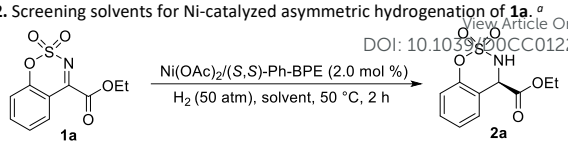


Figure 1. The structures of chiral bisphosphine ligands.

The solvent effect was then inspected for this $Ni(OAc)_2$/(*S*,*S*)-Ph-BPE-catalyzed asymmetric hydrogenation of model substrate **1a**. High conversions and excellent enantioselectivities were obtained in HFIP, TFE (trifluoroethanol) and CH_2Cl_2 (90%->99% conversions, 96% ee, Table 2, entries 1-2, 6). Although 96% ee was provided in MeOH, poor conversion was detected (Table 2, entry 3). This hydrogenation did not proceed in ^{i}PrOH, 1,4-dioxane, THF (tetrahydrofuran) (Table 2, entries 4-5, 8). Poor reactivity and enantioselectivity was afforded in toluene (7% conversion, 30% ee, Table 2, entry 7). Therefore, HFIP was found as the best solvent for this Ni-catalyzed hydrogenation.

Once the optimized reaction conditions were established, a wide range of cyclic N-sulfonyl ketimino esters were inspected to

Table 2. Screening solvents for Ni-catalyzed asymmetric hydrogenation of **1a**. [a]

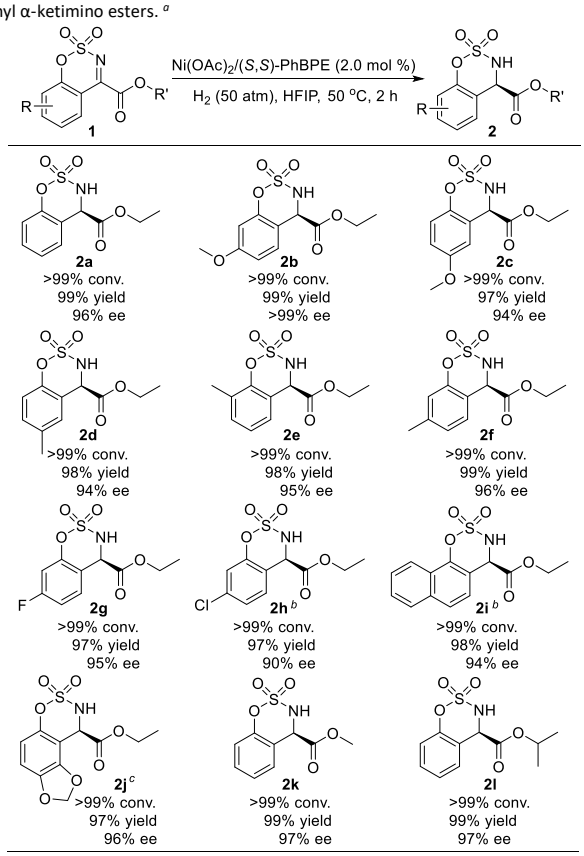


Entry	Solvent	Conv. (%)[b]	Ee (%)[c]
1	HFIP	>99	96
2	TFE	97	96
3	MeOH	10	96
4	^{i}PrOH	NR	NA
5	1,4-dioxane	NR	NA
6	CH_2Cl_2	90	96
7	toluene	7	30
8	THF	NR	NA

[a] Unless otherwise noted, all reactions were carried out with a $Ni(OAc)_2$/(*S*,*S*)-Ph-BPE/**1a** (0.05 mmol) ratio of 1:1.1:50 at 50 °C in 0.7 mL solvent under 50 atm H_2 for 2 h. [b] Determined by ^1H NMR analysis. [c] Determined by HPLC on a chiral phase.

investigate the substrate scope. These results were summarized in Scheme 2. The cyclic N-sulfonyl ketimino ethyl esters containing electron-donating (**1b**-**1f**, **1j**) or electron-withdrawing (**1g**-**1h**) substituents on the benzo ring were hydrogenated well to give the products (**2b**-**2h**, **2j**) with 97%-99% yields and 90%->99% ee. The naphthalene-fused ketimino ethyl ester **1i** also worked efficiently with 98% yield and 94% ee. Further investigation on the ester group indicated that there is almost no effect on the reactivity and enantioselectivity of the substrates

Scheme 2. Substrate scope study for Ni-catalyzed asymmetric hydrogenation of cyclic N-sulfonyl α-ketimino esters. [a]

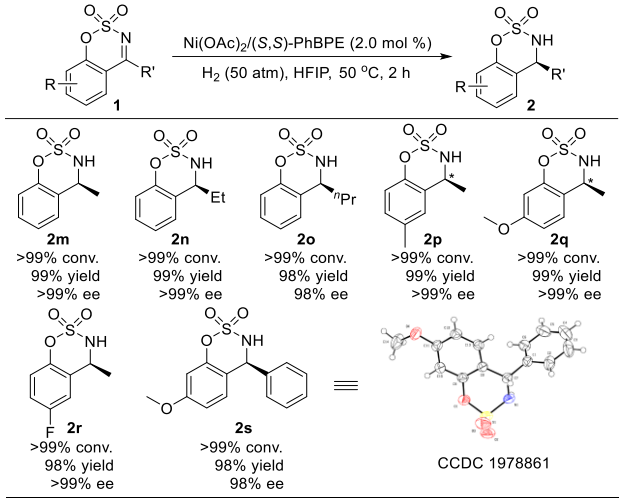


[a] Unless otherwise noted, all reactions were carried out with a $Ni(OAc)_2$/(*S*,*S*)-Ph-BPE/substrate **1** (0.05 mmol) ratio of 1:1.1:50 at 50 °C in 0.7 mL HFIP under 50 atm H_2 for 2 h. Conversion was determined by ^1H NMR analysis. The yield was isolated yield. Ee was determined by HPLC on a chiral phase. [b] S/C = 50, 3 h. [c] S/C = 20, 4 h.

with different ester groups. The substrates with methyl ester group **1k** or isopropyl ester group **1l** were hydrogenated well, affording products **2k**-**2l** with 99% yield and 97% ee.

Encouraged by the above excellent performance of this catalytic system, we began to explore other cyclic N-sulfonyl ketimines for further substrate scope study. By varying the ester group to alkyl or aryl group, a series of cyclic N-sulfonyl ketimines were evaluated (Scheme 3). When the ester group was replaced by methyl, ethyl and *n*-propyl group, the expected products **2m**-**2o** were afforded with 98%-99% yields and 98%->99% ee. The substrates (**1p**-**1r**) bearing substituted group on the benzo ring with diverse electronic properties and positions were employed well. Moreover, when the alkyl group was changed to phenyl group, the substrate **1s** was applied to obtain product **2s** with 98% yield and 98% ee.[23a]

Scheme 3. Substrate scope study for Ni-catalyzed asymmetric hydrogenation of cyclic N-sulfonyl ketimines.[a]

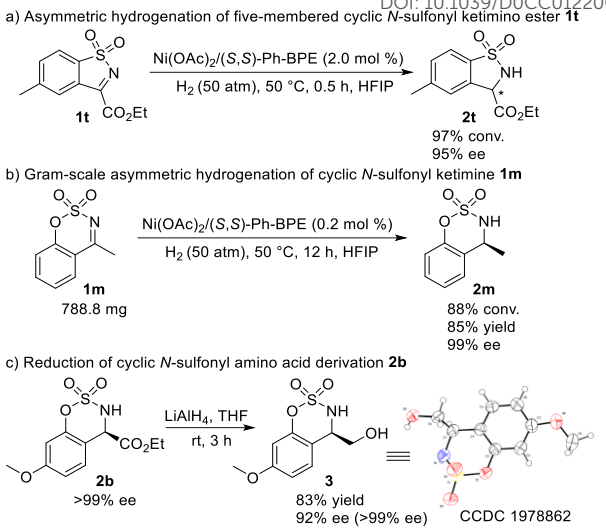


[a] Unless otherwise noted, all reactions were carried out with a $Ni(OAc)_2$/(*S*,*S*)-Ph-BPE/substrate **1** (0.05 mmol) ratio of 1:1.1:50 at 50 °C in 0.7 mL HFIP under 50 atm H_2 for 2 h. Conversion was determined by ^1H NMR analysis. The yield was isolated yield. Ee was determined by HPLC on a chiral phase.

To our delight, the five-membered cyclic N-sulfonyl ketimino ester **1t** was also hydrogenated well to obtain product **2t** with 97% conversion and 95% ee within 0.5 h (Scheme 4a), the corresponding acid derivative may be used as a chiral auxiliary in asymmetric synthesis.[7] Moreover, the gram-scale asymmetric hydrogenation of substrate **1m** was proceeded efficiently with only 0.2 mol% catalyst, affording product **2m** with 88% conversion, 85% yield and 99% ee (Scheme 4b). To demonstrate the utility of this methodology, the hydrogenation product **2b** was reduced by $LiAlH_4$ to cyclic N-sulfonyl amino alcohol **3** in 83% yield with little erosion of ee value (92% ee) at room temperature, which can be improved to >99% ee through simple recrystallization in CH_2Cl_2 and hexane (Scheme 4c).[23b]

Subsequently, the nonlinear effect experiments were conducted, a series of Ni-catalyzed asymmetric hydrogenation of model substrate **1a** were conducted in the presence of the (*S*,*S*)-Ph-BPE ligand with varying enantiopurity. As shown in Figure 2 left, a positive nonlinear effect was observed, which may arise the auto association of these

Scheme 4. Asymmetric hydrogenation of five-membered ketimino ester **1t**, ketimine **1m** and transformation.



initial chiral species.[24] However, linear effect was discovered in the reduction of substrate cyclic N-sulfonyl ketamine **1m** (Figure 2, right), which disclosed that there should be no catalyst self-aggregation or ligand-substrate agglomeration in this catalytic system.[24] These results exhibited that it is possible to have different catalytic species in the hydrogenation of these two kinds of substrates.

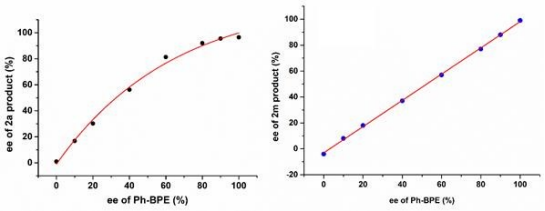


Figure 2. Ni-catalyzed hydrogenation of substrate **1a** (left) and **1m** (right) using ligand (*S*,*S*)-Ph-BPE with different ee values.

In summary, we developed an efficient Ni-catalyzed asymmetric hydrogenation of cyclic N-sulfonyl ketimino esters and cyclic N-sulfonyl ketimines to prepare a series of chiral α-monosubstituted α-amino acid derivatives and chiral amine derivatives with excellent results (97%-99% yields, 90%->99% ee). Additionally, this asymmetric hydrogenation was performed well on gram-scale without loss of enantioselectivity. Different nonlinear effects were observed with these substrates, which disclosed that there may be different nickel catalytic species in these reaction systems.

We are grateful for financial support from the Natural Science Foundation of Jiangsu Province (Grant No. BK20190213), Wuhan Morning Light Plan of Youth Science and Technology (Grant No. 2017050304010307), Shenzhen Science and Technology Innovation Committee (Grant No. KQTD20150717103157174).

Notes and references

[1] (a) Unnatural Amino Acids: Methods and Protocols, ed. L. Pollegioni and S. Servi, Springer, New York, 2012, pp. 1–249. (b) Amino Acids, Peptides and Proteins in Organic Chemistry, ed. A. B. Hughes, Wiley-VCH, Weinheim, 2009, vol. 1, pp. 495–526. (c) A. Viso, R. F. de la Pradilla, A. Garcia, A. Flores, *Chem. Rev.* 2005, **105**, 3167–3196. (d) J. Wang, L. Zhang, H. Jiang, K. Chen, H. Liu, *CHIMIA* 2011, **65**, 919–924.

[2] (a) M. R. Zamora, M. R. Nicolls, T. N. Hodges, J. Marquesen, T. Astor, T. Grazia, D. Weill, *Am. J. Transplant.* 2004, **4**, 1635–1642. (b) X. Wang, H. Yang, X. Zhang, X. Cui, S. Wang, L. Liu, *J. Pharm. Pharm. Sci.*, 2017, **20**, 168–183.

[3] G. L. La Rosa, L. Lupo, D. Giuffrida, D. Gullo, R. Vigneri, A. Belfiore, *Ann. Intern. Med*. 1995, **122**, 1–8.

[4] G. Ruiz-Hurtado, L. M. Ruilope, *Eur. Heart J.* 2017, **38**, 3318–3320.

[5] C. Y. Pan, W. Yang, C. Tou, I. Gause-Nilsson, J. Zhao, *Diabetes Metab. Res. Rev*. 2012, **28**, 268–275.

[6] J. C. Song, C. M. White, *Clin. Pharmacokinet.* 2002, **41**, 207–224.

[7] (a) K. C. Majumdar, S. Mondal, *Chem. Rev.* 2011, **111**, 7749–7773. (b) K. H. Ahn, H.-H. Baek, S. J. Lee, C.-W. Cho, *J. Org. Chem.* 2000, **65**, 7690–7696.

[8] (a) M. K. Ghorai, K. Das, A. Kumar, *Tetrahedron Lett*. 2007, **48**, 2471–2475. (b) C. Cativiela, M. D. Díaz-de-Villegas, *Tetrahedron: Asymmetry* 1998, **9**, 3517–3599. (c) R. C. Atkinson, F. Fernandez-Nieto, J. M. Rosellý, J. Clayden, *Angew. Chem. Int. Ed.* 2015, **54**, 8961–8965. (d) J. L. Vicario, D. Badia, L. Carrillo, J. Etxebarria, *Curr. Org. Chem.* 2003, **7**, 1775–1792. (e) Y. Deng, H. Qiu, H. D. Srinivas, M. P. Doyle, *Curr. Org. Chem.* 2016, **20**, 61–81. (f) A. Saitoh, K. Achiwa, K. Tanaka, T. Morimoto, *J. Org. Chem.* 2000, **65**, 4227–4240.

[9] (a) T. Nemoto, T. Harada, T. Matsumoto, Y. Hamada, *Tetrahedron Lett.* 2007, **48**, 6304–6307. (b) X. Huo, J. Fu, X. He, J. Chen, F. Xie, W. Zhang, *Chem. Commun.* 2018, **54**, 599–602. (c) Z. Lu, S. Ma, *Angew. Chem. Int. Ed.* 2008, **47**, 258–297. (d) K. Yao, Q. Yuan, X. Qu, Y. Liu, D. Liu, W. Zhang, *Chem. Sci.* 2019, **10**, 1767–1772. (e) L. Wei, Q.-H. Li, C.-J. Wang, *J. Org. Chem.* 2018, **83**, 11814–11824. (f) H.-C. Liu, L. Wei, R. Huang, H.-Y. Tao, H. Cong, C.-J. Wang, *Org. Lett.* 2018, **20**, 3482–3486. (g) K. Liu, Y. Xiong, Z.-F. Wang, H.-Y. Tao, C.-J. Wang, *Chem. Commun.* 2016, **52**, 9458–9461. (h) Q.-H. Li, L. Wei, C.-J. Wang, *J. Am. Chem. Soc.* 2014, **136**, 8685–8692.

[10] (a) B. Zhou, K. Li, C. Jiang, Y. Lu, T. Hayashi, *Adv. Synth. Catal.* 2017, **359**, 1969–1975. (b) M. Quan, G. Yang, F. Xie, I. D. Gridnev, W. Zhang, *Org. Chem. Front.* 2015, **2**, 398–402. (c) R. Takechi, T. Nishimura, *Org. Biomol. Chem.* 2015, **13**, 4918–4924. (d) Z. Wang, M.-H. Xu, *Org. Biomol. Chem.* 2018, **16**, 4633–4640. (e) H. Wang, T. Jiang, M.-H. Xu, *J. Am. Chem. Soc.* 2013, **135**, 971–974. (f) M. Quan, X. Wang, L. Wu, I. D. Gridnev, G. Yang, W. Zhang, *Nat. Commun*. 2018, **9**, 2258. (g) J. Chen, X. Lu, W. Lou, Y. Ye, H. Jiang, W. Zeng, *J. Org. Chem.* 2012, **77**, 8541–8548.

[11] M. Hatano, H. Okamoto, T. Kawakami, K. Toh, H. Nakatsuji, A. Sakakura, K. Ishihara, *Chem. Sci.* 2018, **9**, 6361–6367.

[12] (a) L. Wei, Q. Zhu, S.-M. Xu, X. Chang, C.-J. Wang, *J. Am. Chem. Soc.* 2018, **140**, 1508–1513. (b) L. Wei, L. Xiao, C.-J. Wang, *Adv. Synth. Catal.* 2018, **360**, 4715–4719. (c) L. Wei, S.-M. Xu, Q. Zhu, C. Che, C.-J. Wang, *Angew. Chem. Int. Ed.* 2017, **56**, 12312–12316. (d) B. M. Trost, X. Ariza, *Angew. Chem. Int. Ed.* 1997, **36**, 2635–2637. (e) B. M. Trost, K. Dogra, *J. Am. Chem. Soc.* 2002, **124**, 7256–7257.

[13] (a) T. Ooi, M. Takeuchi, M. Kameda, K. Maruoka, *J. Am. Chem. Soc.* 2000, **122**, 5228–5229. (b) A.-s. Jew, Y.-J. Lee, J. Lee, M. J. Kang, B.-S. Jeong, J.-H. Lee, M.-S. Yoo, M.-J. Kim, S.-h. Choi, J.-M. Ku, H.-g. Park, *Angew. Chem. Int. Ed.* 2004, **43**, 2382–2385. (c) T. Ooi, E. Tayama, K. Maruoka, *Angew. Chem. Int. Ed.* 2003, **42**, 579–582. (d) T. Ooi, M. Takeuchi, D. Kato, Y. Uematsu, E. Tayama, D. Sakai, K. Maruoka, *J. Am. Chem. Soc*. 2005, **127**, 5073–5083.

[14] (a) M. Marigo, K. Juhl, K. A. Jørgensen, *Angew. Chem. Int. Ed.* 2003, **42,** 1367–1369. (b) S. Saaby, M. Bella, K. A. Jørgensen, *J. Am. Chem. Soc.* 2004, **126**, 8120–8121. (c) X. Liu, H. Li, L. Deng, *Org. Lett.* 2005, **7**, 167–169. (d) P. M. Pikho, A. Pohjakallio, *Synlett.* 2004, 2115–2118. (e) X. Xu, T. Yabuta, P. Yuan, Y. Takemoto, *Synlett.* 2006, 137–140.

[15] (a) C. Shen, Y. Yang, L. Wei, W.-W. Dong, L. W. Chung, C.-J. Wang, *iScience*, 2019, **11**, 146–159. (b) X. Fang, C.-J. Wang, *Org. Biomol. Chem.* 2018, **16**, 2591–2601. (c) J. Adrio, J. C. Carretero, *Chem. Commun.* 2014, **50**, 12434–12446. (d) R. Narayan, M. Potowski, Z.-J. Jia, A. P. Antonchick, H. Waldmann, *Acc. Chem. Res.* 2014, **47**, 1296–1310. (e) J. Adrio, J. C. Carretero, *Chem. Commun.* **2011**, **47**, 6784–6794. (f) C. Nájera, J. M. Sansano, *Angew. Chem. Int. Ed.* 2005, **44**, 6272–6276.

[16] For some reviews, see: (a) W. S. Knowles, *Acc. Chem. Res.* 1983, **16**, 106–112. (b) R. Noyori, H. Takaya, *Acc. Chem. Res*. 1990, **23**, 345–350. (c) W. Tang, X. Zhang, *Chem. Rev*. 2003, **103,** 3029–3070. (d) H.-U. Blaser, C. Malan, B. Pugin, F. Spindler, H. Steiner, M. Studer, *Adv. Synth. Catal*. 2003, **345**, 103–151. (e) X. Cui, K. Burgess, *Chem. Rev*. 2005, **105**, 3272–3296. (f) A. J. Minnaard, B. L. Feringa, L. Lefort, J. G. de Vries, *Acc. Chem. Res*. 2007, **40**, 1267–1277. (g) W. Zhang, Y. Chi, X. Zhang, *Acc. Chem. Res.* 2007, **40**, 1278–1290. (h) N. B. Johnson, I. C. Lennon, P. H. Moran, J. A. Ramsden, *Acc. Chem. Res.* 2007, **40**, 1291–1299. (i) Y.-G. Zhou, *Acc. Chem. Res*. 2007, **40**, 1357–1366. (j) S. J. Roseblade, A. Pfaltz, *Acc. Chem. Res*. 2007, **40**, 1402–1411. (k) J.-H. Xie, S.-F. Zhu, Q.-L. Zhou, *Chem. Rev*. 2011, **111**, 1713–1760. (l) D.-S. Wang, Q.-A. Chen, S.-M. Lu, Y.-G. Zhou, *Chem. Rev*. 2012, **112**, 2557–2590. (m) J.-H. Xie, S.-F. Zhu, Q.-L. Zhou, *Chem. Soc. Rev*. 2012, **41**, 4126–4139. (n) Q.-A. Chen, Z.-S. Ye, Y. Duan, Y.-G. Zhou, *Chem. Soc. Rev.* 2013, **42**, 497–511. (o) J. J. Verendel, O. Pamies, M. Dieguez, P. G. Andersson, *Chem. Rev*. 2014, **114**, 2130–2169. (p) Z. Zhang, N. A. Butt, W. Zhang, *Chem. Rev*. 2016, **116**, 14769–14827. (q) J. Xie, Q. Zhou, *Acta Chim. Sina.* 2012, **70**, 1427–1438. (r) S.-M. Lu, X.-W. Han, Y.-G. Zhou, *Chin. J. Org. Chem.* 2005, **25**, 634–640.

[17] (a) Y. Hamada, Y. Koseki, T. Fujii, T. Maeda, T. Hibino, K. Makino, *Chem. Commun*. 2008, 6206–6208. (b) T. Hibino, K. Makino, T. Sugiyama, Y. Hamada, *ChemCatChem*. 2009, **1**, 237–240.

[18] M. Shevlin, M. R. Friedfeld, H. Sheng, N. A. Pierson, J. M. Hoyt, L.-C. Campeau, P. J. Chirik, *J. Am. Chem. Soc.* 2016, **138**, 3562–3569.

[19] (a) P. Yang, H. Y. Xu, J. Zhou, *Angew. Chem. Int. Ed.* 2014, **53**, 12210–12213. (b) S. Y. Guo, P. Yang, J. Zhou, *Chem. Commun.* 2015, **51**, 12115–12117. (c) H. Y. Xu, P. Yang, P. Chuanprasit, H. Hirao, J. Zhou, *Angew. Chem. Int. Ed.* 2015, **54**, 5112–5116. (d) P. Yang, L. H. Lim, P. Chuanprasit, H. Hirao, J. Zhou, *Angew. Chem. Int. Ed.* 2016, **55**, 12083–12087. (e) S. Guo, J. Zhou, *Org. Lett.* 2016, **18**, 5344–5347. (f) X. Zhao, H. Xu, X. Huang, J. Zhou, *Angew. Chem. Int. Ed.* 2019, **58**, 292–296.

[20] (a) B. Li, J. Chen, Z. Zhang, I. D. Gridnev, W. Zhang, *Angew. Chem. Int. Ed.* 2019, **58**, 7329–7334. (b) Y. Hu, J. Chen, B. Li, Z. Zhang, I. D. Gridnev, W. Zhang, *Angew. Chem. Int. Ed.* 2020, **59**, 5371–5375.

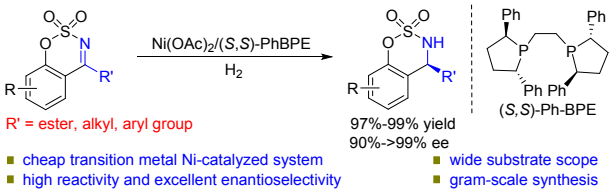
[21] (a) W. Gao, H. Lv, T. Zhang, Y. Yang, L. W. Chung, Y.-D. Wu, X. Zhang, *Chem. Sci.* 2017, **8**, 6419–6422. (b) X. Li, C. You, S. Li, H. Lv, X. Zhang, *Org. Lett.* 2017, **19**, 5130–5133. (c) J. Long, W. Gao, Y. Guan, H. Lv, X. Zhang, *Org. Lett.* 2018, **20**, 5914–5917. (d) Y.-Q. Guan, Z. Han, X. Li, C. You, X. Tan, H. Lv, X. Zhang, *Chem. Sci.* 2019, **10**, 252-256. (e) Y. Liu, Z. Yi, X. Tan, X.-Q. Dong, X. Zhang, *iScience*, 2019, **19**, 63–73. (f) Z. Han, G. Liu, X. Zhang, A. Li, X.-Q. Dong, X. Zhang, *Org. Lett.* 2019, **21**, 3923–3926.

[22] (a) Y.-Q. Wang, C.-B. Yu, D.-W. Wang, X.-B. Wang, Y.-G. Zhou, *Org. Lett.* 2008, **10**, 2071–2074. (b) C.-B. Yu, D.-W. Wang, Y.-G. Zhou, *J. Org. Chem.* 2009, **74**, 5633–5635. (c) S. Kang, J. Han, E. S. Lee, E. B. Choi, H.-K. Lee, *Org. Lett.* 2010, **12**, 4184–4187.

[23] (a) The X-ray crystal data of compound **2s** has been deposited with the Cambridge Crystallographic Data Centre as no. CCDC 1978861. (b) The X-ray crystal data of compound **3** has been deposited with the Cambridge Crystallographic Data Centre as no. CCDC 1978862. The absolute configuration of compound **2b** is determined as *R* by the deduction from compound **3**.

[24] (a) D. Guillaneux, S.-H. Zhao, O. Samuel, D. Rainford, H. B. Kagan, *J. Am. Chem. Soc.* 1994, **116**, 9430–9439. (b) C. Girard, H. B. Kagan, *Angew. Chem. Int. Ed.* 1998, **37**, 2922–2959.

View Article Online
DOI: 10.1039/D0CC01220C



Efficient Ni-catalyzed asymmetric hydrogenation of cyclic N-sulfonyl ketimino esters and ketimines was successfully developed to prepare a series of chiral α-monosubstituted α-amino acid derivatives and chiral amine derivatives with excellent results (97%-99% yields, 90%->99% ee).