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Hydrogenation of Carbonyl Derivatives Catalysed by Manganese Complexes Bearing Bidentate Pyridinyl-Phosphine Ligands

Duo Wei,^a Antoine Bruneau-Voisine,^a Téo Chauvin,^a Vincent Dorcet,^b Thierry Roisnel,^b Dmitry A. Valyaev,^c Noël Lugan^c and Jean-Baptiste Sortais^{a,c,d,*}

^a Institut des Sciences Chimiques de Rennes, UMR 6226 CNRS-Université de Rennes 1, Team Organometallics: Materials and Catalysis, 263 av. du Général Leclerc, 35042 Rennes Cedex, France

^b Institut des Sciences Chimiques de Rennes, UMR 6226 CNRS-Université de Rennes 1, Centre de Diffraction X, 263 av. du Général Leclerc, 35042 Rennes Cedex, France

^c LCC-CNRS, Université de Toulouse, INPT, UPS, 205 route de Narbonne 31077 Toulouse Cedex 4, France. Email : jean-baptiste.sortais@lcc-toulouse.fr

^d Institut Universitaire de France, 1 rue Descartes, 75231 Paris Cedex 05, France.

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Abstract. Manganese(I) catalysts incorporating readily available bidentate 2-aminopyridinyl-phosphine ligands achieve a high efficiency in the hydrogenation of carbonyl compounds, significantly better than parent ones based on more elaborated and expensive tridentate 2,6-(diaminopyridinyl)-diphosphine ligands. The reaction proceeds with low catalyst loading (0.5 mol%) under mild conditions (50 °C) with yields up to 96%.

Keywords: hydrogenation; manganese; ketones; reduction; P,N-ligands

Hydrogenation with molecular dihydrogen is a clean, atom-economic and efficient reaction that has drawn a huge interest for more than a century from the Nobel Prize of Sabatier in 1912 for heterogeneous hydrogenation to the one of Noyori and Knowles in 2001 for asymmetric hydrogenation.^[1] Homogeneous hydrogenation catalysts are usually complexes based on late transition metals including ruthenium, rhodium, iridium, nickel and palladium. In the last decade, iron has emerged as a powerful sustainable alternative candidate in catalysed reduction reactions, as it is the most abundant and inexpensive transition metal.^[2] Actually, the level of the activity, and chemo- and enantioselectivity of iron catalytic systems is now comparable to the ones involving noble transition metals.^[3] Manganese, being the third most abundant transition metals after iron and titanium, has recently emerged as suitable transition metal for the design of efficient hydrogenation catalysts^[4] starting with a seminal contribution of Beller in 2016 using the Mn^I complex **I** featuring a tridentate bis(phosphino)amine ligand (Scheme 1).^[5]

Soon after, a series of parent Mn^I complexes exhibiting a variety of tridentate ligands including nitrogen and phosphorus donor fragments has been successfully applied in hydrogenation^[6] and related hydrogen borrowing reactions,^[7] selected representative examples being shown in Scheme 1.

Scheme 1. Representative examples of manganese catalysts for redox reactions.

In the course of our investigations directed toward manganese catalysed reduction reactions,^[8] we first demonstrated that the PN³P manganese complex **IV** bearing a 2,6-(diaminopyridinyl)-diphosphine ligand was suitable for the hydrogenation of carbonyl derivatives,^[6c] yet with moderate activity compared to PN⁵P analogue **III** developed by Kempe^[6a] and based on the 2,6-(diaminotriazinyl)-diphosphine ligand. Searching for simpler catalytic system, we found later that the manganese complex **VII** featuring a bidentate picolylamine ligand was significantly more active^[6d] than Beller's tridentate dipicolylamine complex **V**^[6b] in the case of hydrogen transfer reaction using 2-propanol as the reductant. In the meantime, Pidko and Beller showed that the manganese complex **VI** bearing bidentate phosphinoamine ligand was as active as **I** for the hydrogenation of esters.^[5b, 9] In the present contribution, we demonstrate that simple Mn^I complexes bearing readily available phosphino-pyridinyl PN bidentate ligands can achieve a very high efficiency in the hydrogenation of carbonyl compounds.

The ligands R₂P–X–Py (**L1**: R = *i*Pr, X = NH; **L2**: R = Ph, X = NH; **L3**: R = Ph, X = CH₂) and Ph₂P–CH₂–Qn (**L4**) were obtained in high yield starting from the appropriate chlorophosphines R₂PCl and 2-aminopyridine (**L1**, **L2**),^{[10],[11]} 2-picoline (**L3**),^[12] or 2-methylquinoline (**L4**),^[13] respectively, according to literature procedures. The corresponding complexes Mn(CO)₃Br(κ²P,N-**L1-L4**) (**1-4**) (Fig. 1) were readily obtained in excellent yield (87-91%) upon simple heating of an equimolar mixture of Mn(CO)₅Br and the given ligand in toluene at 100 °C overnight. They were fully characterised by IR and NMR spectroscopy, high-resolution mass spectrometry and elemental analysis, and their solid-state structures were determined by single-crystal X-ray diffraction.^[14] Perspective views of the complexes are displayed on Figure 2 for complex **2**, and on Figures S15, S17 and S18 for complexes **1**, **3**, and **4**, respectively. All complexes show a typical octahedral environment for the Mn center, the **L1-L4** ligands being coordinated in a κ²P,N mode and the three carbonyl ligands being in facial position.

Figure 1. Manganese complexes synthesised for this study.

Figure 2. Perspective view of complex **2** with thermal ellipsoids drawn at the 50% probability level.

Table 1. Optimization of the reaction parameters

Entry	Catalyst (mol%)	Base (mol%)	Temp. (°C)	Solvent	Yield ^b
1	1 (5)	<i>t</i> BuOK (10)	110	toluene	> 98
2	1 (1)	<i>t</i> BuOK (2)	110	toluene	> 98
3	1 (1)	<i>t</i> BuOK (2)	80	toluene	65
4	2 (1)	<i>t</i> BuOK (2)	80	toluene	90
5	3 (1)	<i>t</i> BuOK (2)	80	toluene	15
6	4 (1)	<i>t</i> BuOK (2)	80	toluene	16
7	2 (1)	KHMDS (2)	80	toluene	> 98
8	2 (0.5)	KHMDS (1)	80	toluene	81
9	2 (0.5)	KHMDS (1)	80	<i>t</i> -amyl alcohol	76
10	2 (0.5)	KHMDS (2)	80	toluene	95
11	2 (0.1)	KHMDS (1)	80	toluene	43
12	2 (0.5)	KHMDS (2)	50	toluene	93
13	2 (0.5)	KHMDS (2)	50	<i>t</i> -amyl alcohol	51
14	2 (0.5)	KHMDS (2)	30	toluene	44
15	-	KHMDS (2)	50	toluene	0
16	2 (0.5)	-	50	toluene	0
17 ^c	2 (0.5)	KHMDS (2)	80	toluene	93

^a Typical conditions: in an autoclave, **2** (0.5 mol%), toluene (4 mL), ketone (2 mmol), KHMDS (2 mol%), H₂ (50 bar) were added in this order. ^b Yield determined by GC and ¹H

NMR. $^{\circ}$ 300 equiv. of Hg (vs **2**) were added before H₂ in the reaction mixture.

The catalytic activity of the new complexes **1-4** was then evaluated for the reduction of ketones under hydrogenation conditions (Table 1). Under the previously optimized reaction conditions determined for the PN³P catalyst **IV**,^[6c] *i.e.* complex **1** (5 mol%), *t*BuOK (10 mol%) as the base, toluene, 110 °C, H₂ (50 bar), 22 h, a full conversion of acetophenone **a1** to the corresponding alcohol **b1** was obtained (entry 1). The catalyst loading could be reduced to 1 mol% without any degradation of the activity (Table 1, entry 2). The performance of the four complexes was then compared at 80 °C (entries 3-6): complex **1** exhibiting the amino-bridged diisopropylphosphino-pyridinyl bidentate ligand **L1** gave a moderate conversion (65%), whereas the diphenylphosphino derivative **2** gave the alcohol in 90% yield. Disappointingly, complexes **3** and **4** featuring the methylene-bridged PN bidentate ligands **L3** and **L4** led to low conversion (15 and 16% respectively, entries 5 and 6). The nature of the base was optimized using **2** as pre-catalyst. KHMDS (potassium bis(trimethylsilyl)amide) appeared to be the best one leading to a full conversion with 1 mol% of complex and 2 mol% of base at 80 °C in toluene (entry 7). With this base, the catalyst loading could be even decreased to 0.5 mol% (entries 8-10). With 0.1 mol% of catalyst a TON of 430 was achieved (entry 11). The temperature could also be lowered to 50 °C without significant loss of efficiency (entries 12-13). At 30 °C, however, the conversion dropped to 44% (entry 14). The influence of the solvent and of the pressure was also evaluated (see ESI, Tables S1 and S2). Notably, *tert*-amyl alcohol was found to be suitable for this reaction at 80 °C, as an alternative greener solvent (entries 9 and 13).^[15] Control experiment showed that the presence of Hg has no influence on the reaction (entry 17 vs entry 10). Eventually, the optimal condition selected were catalyst **2** (0.5 mol%), KHMDS (2 mol%), toluene, 50 bar of hydrogen, 20 h (entry 10).

Next, we explored the substrates scope amenable for the PN manganese precatalyst **2** in hydrogenation (Table 2). In general, arylketones bearing both electron withdrawing and electron donating substituents were reduced in very good yields. In the case of halogenated ketones, fluoro- and bromo-derivatives (**a5**, **a7**) were well tolerated with low catalyst loading, whereas chloro- and iodo-substituted ketones (**a6**, **a8**) were not fully reduced, even under slightly forcing conditions. Steric hindrance had a noticeable influence as increasing the length and the branching of the alkyl chains from methyl (**a1**), ethyl (**a13**) to isopropyl (**a14**) induced a significant drop in the conversion (93% for **b1**, 97% for **b13** to 35% for **b14**). In line with these observations 2',4',6'-trimethylacetophenone **a15** was not reduced with this system. Among the various coordinating functional groups, primary amines **a12**, benzofurane **a16**, and pyridine **a17** were tolerated, but required a higher

catalyst loading. Conversely, cyano-derivatives **a10** was reduced in very low yield, and nitro **b11** and thiophene **b18** moieties completely inhibited the reaction.^[16] A series of aliphatic and cyclic ketones was reduced smoothly (**b19-b23**). Isolated tri-substituted C=C double bond in **a23** remained completely intact during the hydrogenation process. In order to confirm this selectivity, a series of competitive reduction of acetophenone, in the presence of 1-decene, 5-decene and 5-decyne, respectively, were conducted. In all the cases, the reduction of the ketone proceeds without the reduction of the unsaturated C-C bond (See Table S3). Finally, *para*-substituted benzaldehydes (**a24-a26**) were also reduced to the corresponding benzylic alcohols in high yields showing the tolerance toward ester (**b25**) and amide (**b26**) groups.

Table 2. Scope of the hydrogenation of carbonyl derivatives under the catalysis of **2**.^a

^a General conditions: ketone (2 mmol), H₂ (50 bar), **2** (0.5 mol%), KHMDS (2 mol%), toluene (4 mL, 0.5 mol.L⁻¹),

50 °C, 20 h. Conversion determined by ^1H NMR, isolated yield in parentheses. ^b **2** (0.5 mol%), KHMDS (2 mol%), 80 °C. ^c **2** (1 mol%), *t*BuOK (2 mol%), 80 °C. ^d **2** (5 mol%), *t*BuOK (10 mol%), 80 °C. ^e **2** (1 mol%), *t*BuOK (2 mol%), 50 °C.

In the case of α,β -unsaturated 4-phenylbut-3-en-2-one **a27**, under the standard conditions, a 13:87 mixture of fully reduced product **b19** and ketone **a19** was obtained. Interestingly, under milder conditions, at 30 °C, the saturated ketone **a29** was obtained selectively, while under harsher ones, at 80 °C, the saturated alcohol **b19** was obtained quantitatively (Scheme 2, i and ii). Similarly, chalcone **a28** could be reduced selectively to 1,3-diphenylpropan-1-one **a29** or to 1,3(diphenylpropan-1-ol **b28** (Scheme 2, iii and iv). The reduction of (*R*)-carvone **a30**, bearing both a conjugated and a non-conjugated C=C bond, under mild conditions, led to the formation of a mixture of isomer of dihydrocarvone^[17] **a31** and **a32**. Under harsher conditions, dihydrocarveol^[18] **b30** was obtained in high yield (87%). In both cases, the non-conjugated C=C bond remained intact. Compared to the reduction of α,β -unsaturated aldehydes by aliphatic PNP manganese catalysts **1**,^[5a] where the unsaturated alcohols were produced selectively, and to the reduction of α,β -unsaturated esters,^[5b] where solely saturated alcohols were obtained, the present catalytic system allows to reduce exclusively the conjugated C=C double bond, supplementing the previously described ones.

- i) **2** (0.5 mol%), KHMDS (2 mol%), 30 °C, H_2 (50 bar), toluene, 18 h
 ii) **2** (5 mol%), *t*BuOK (10 mol%), 80 °C, H_2 (50 bar), toluene, 18 h
 iii) **2** (2 mol%), *t*BuOK (5 mol%), 80 °C, H_2 (50 bar), toluene, 18 h
 iv) **2** (5 mol%), *t*BuOK (10 mol%), 100 °C, H_2 (50 bar), toluene, 22 h

- v) **2** (1 mol%), *t*BuOK (2 mol%), 80 °C, H_2 (50 bar), toluene, 18 h
 vi) **2** (5 mol%), *t*BuOK (10 mol%), 100 °C, H_2 (50 bar), toluene, 18 h

Scheme 2. Selective reduction of conjugated enones.

In conclusion, a series four Mn^{I} complexes bearing readily available phosphino-pyridinyl PN bidentate ligands have been prepared, fully characterized, and their catalytic activity was evaluated in the hydrogenation of aldehydes and ketones. The complex $\text{Mn}(\text{CO})_3\text{Br}(\kappa^2\text{P},\text{N}-\text{Ph}_2\text{PN}(\text{H})\text{Py})$ (**2**) showed good performances for the hydrogenation of carbonyl derivatives under mild conditions with low catalyst loading and satisfying functional group tolerance, compared to the most active catalytic systems.^[6a, 6e] In terms of catalyst design and taking the PN^3P Mn^{I} complex **IV** as reference,^[6c] it appears that simplifying the ancillary tridentate ligand to a bidentate ligand by removing one of its wingtip led to a dramatic increase of the activity of resulting catalytic system.^[19] Indeed, the use of the PN Mn^{I} complex **2** allowed reducing the catalyst loading by a factor of ten, and lowering the temperature from 130 °C to 50 °C, still keeping the same level of activity and chemoselectivity.^[6c]

Experimental Section

General procedure for hydrogenation reactions: in an argon filled glove box, an autoclave was charged with complex **2** (5.0 mg, 0.5 mol%) and anhydrous toluene (4.0 mL), followed by ketone (2.0 mmol) and potassium bis(trimethylsilyl)amide (KHMDS, 8.0 mg, 2 mol%), in this order. The autoclave is then charged H_2 (50 bar). The mixture was stirred for 20 hours at 50 °C in an oil bath. The crude residue was purified by column chromatography.

For full experimental details for the synthesis of Mn^{I} complexes and for catalytic products, see the Supporting Information.

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References

- [1] J. G. De Vries, C. J. Elsevier, *The Handbook of Homogeneous Hydrogenation*, WILEY-VCH, Weinheim, 2007.
- [2] a) S. Gaillard, J.-L. Renaud, *ChemSusChem* **2008**, *1*, 505-509; b) R. H. Morris, *Chem. Soc. Rev.* **2009**, *38*, 2282-2291; c) R. H. Morris, *Acc. Chem. Res.* **2015**, *48*, 1494-1502; d) L. C. Misal Castro, H. Li, J.-B. Sortais, C. Darcel, *Green Chem.* **2015**, *17*, 2283-2303; e) D. S. Mérel, M. L. T. Do, S. Gaillard, P. Dupau, J.-L. Renaud, *Coord. Chem. Rev.* **2015**, *288*, 50-68; f) I. Bauer, H.-J. Knölker, *Chem. Rev.* **2015**, *115*, 3170-3387.

- [3] a) R. M. Bullock, *Science* **2013**, *342*, 1054-1055; b) W. Zuo, A. J. Lough, Y. F. Li, R. H. Morris, *Science* **2013**, *342*, 1080-1083.
- [4] a) R. I. Khusnutdinov, A. R. Bayguzina, U. M. Dzhemilev, *Russ. J. Org. Chem.* **2012**, *48*, 309-348; b) R. J. Trovitch, *Synlett* **2014**, *25*, 1638-1642; c) D. A. Valyaev, G. Lavigne, N. Lugan, *Coord. Chem. Rev.* **2016**, *308*, 191-235.
- [5] a) S. Elangovan, C. Topf, S. Fischer, H. Jiao, A. Spannenberg, W. Baumann, R. Ludwig, K. Junge, M. Beller, *J. Am. Chem. Soc.* **2016**, *138*, 8809-8814; b) S. Elangovan, M. Garbe, H. Jiao, A. Spannenberg, K. Junge, M. Beller, *Angew. Chem. Int. Ed.* **2016**, *55*, 15364-15368; c) S. Elangovan, J. Neumann, J.-B. Sortais, K. Junge, C. Darcel, M. Beller, *Nat. Commun.* **2016**, *7*, 12641; d) M. Peña - López, P. Piehl, S. Elangovan, H. Neumann, M. Beller, *Angew. Chem. Int. Ed.* **2016**, *55*, 14967-14971; e) M. Andérez - Fernández, L. K. Vogt, S. Fischer, W. Zhou, H. Jiao, M. Garbe, S. Elangovan, K. Junge, H. Junge, R. Ludwig, M. Beller, *Angew. Chem. Int. Ed.* **2017**, *56*, 559-562.
- [6] a) F. Kallmeier, T. Irrgang, T. Dietel, R. Kempe, *Angew. Chem. Int. Ed.* **2016**, *55*, 11806-11809; b) M. Perez, S. Elangovan, A. Spannenberg, K. Junge, M. Beller, *ChemSusChem* **2017**, *10*, 83-86; c) A. Bruneau-Voisine, D. Wang, T. Roisnel, C. Darcel, J.-B. Sortais, *Catal. Commun.* **2017**, *92*, 1-4; d) A. Bruneau-Voisine, D. Wang, V. Dorcet, T. Roisnel, C. Darcel, J.-B. Sortais, *Org. Lett.* **2017**, *19*, 3656-3659; e) M. B. Widegren, G. J. Harkness, A. M. Z. Slawin, D. B. Cordes, M. L. Clarke, *Angew. Chem. Int. Ed.* **2017**, *56*, 5825-5828; f) F. Bertini, M. Glatz, N. Gorgas, B. Stöger, M. Peruzzini, L. F. Veiros, K. Kirchner, L. Gonsalvi, *Chem. Sci.* **2017**, *8*, 5024-5029; g) A. Zirakzadeh, S. R. M. M. de Aguiar, B. Stöger, M. Widhalm, K. Kirchner, *ChemCatChem* **2017**, *9*, 1744-1748; h) N. A. Espinosa-Jalapa, A. Nerush, L. J. W. Shimon, G. Leitius, L. Avram, Y. Ben-David, D. Milstein, *Chem. Eur. J.* **2017**, *23*, 5934-5938; i) A. M. Tondreau, J. M. Boncella, *Organometallics* **2016**, *35*, 2049-2052; j) A. M. Tondreau, J. M. Boncella, *Polyhedron* **2016**, *116*, 96-104; k) A. Dubey, L. Nencini, R. R. Fayzullin, C. Nervi, J. R. Khusnutdinova, *ACS Catal.* **2017**, *7*, 3864-3868; l) V. Papa, J. R. Cabrero-Antonino, E. Alberico, A. Spanneberg, K. Junge, H. Junge, M. Beller, *Chem. Sci.* **2017**, *8*, 3576-3585.
- [7] a) M. Mastalir, M. Glatz, N. Gorgas, B. Stöger, E. Pittenauer, G. Allmaier, L. F. Veiros, K. Kirchner, *Chem. Eur. J.* **2016**, *22*, 12316-12320; b) M. Mastalir, M. Glatz, E. Pittenauer, G. Allmaier, K. Kirchner, *J. Am. Chem. Soc.* **2016**, *138*, 15543-15546; c) A. Mukherjee, A. Nerush, G. Leitius, L. J. W. Shimon, Y. Ben David, N. A. Espinosa Jalapa, D. Milstein, *J. Am. Chem. Soc.* **2016**, *138*, 4298-4301; d) A. Nerush, M. Vogt, U. Gellrich, G. Leitius, Y. Ben-David, D. Milstein, *J. Am. Chem. Soc.* **2016**, *138*, 6985-6997; e) J. Neumann, S. Elangovan, A. Spannenberg, K. Junge, M. Beller, *Chem. Eur. J.* **2017**, *23*, 5410-5413; f) A. Bruneau-Voisine, D. Wang, V. Dorcet, T. Roisnel, C. Darcel, J.-B. Sortais, *J. Catal.* **2017**, *347*, 57-62; g) D. H. Nguyen, X. Trivelli, F. Capet, J.-F. Paul, F. Dumeignil, R. M. Gauvin, *ACS Catal.* **2017**, *7*, 2022-2032; h) N. Deibl, R. Kempe, *Angew. Chem. Int. Ed.* **2017**, *56*, 1663-1666; i) F. Kallmeier, B. Dudziec, T. Irrgang, R. Kempe, *Angew. Chem. Int. Ed.* **2017**, *56*, 7261-7265; j) M. Mastalir, E. Pittenauer, G. Allmaier, K. Kirchner, *J. Am. Chem. Soc.* **2017**, *139*, 8812-8815; k) J. O. Bauer, S. Chakraborty, D. Milstein, *ACS Catal.* **2017**, *7*, 4462-4466; l) S. Chakraborty, U. Gellrich, Y. Diskin-Posner, G. Leitius, L. Avram, D. Milstein, *Angew. Chem. Int. Ed. Engl.* **2017**, *56*, 4229-4233.
- [8] a) J. Zheng, S. Chevance, C. Darcel, J.-B. Sortais, *Chem. Commun.* **2013**, *49*, 10010-10012; b) J. Zheng, S. Elangovan, D. A. Valyaev, R. Brousses, V. César, J.-B. Sortais, C. Darcel, N. Lugan, G. Lavigne, *Adv. Synth. Catal.* **2014**, *356*, 1093-1097; c) D. A. Valyaev, D. Wei, S. Elangovan, M. Cavaillès, V. Dorcet, J.-B. Sortais, C. Darcel, N. Lugan, *Organometallics* **2016**, *35*, 4090-4098.
- [9] R. van Putten, E. A. Uslamin, M. Garbe, C. Liu, A. Gonzalez - de - Castro, M. Lutz, K. Junge, E. J. M. Hensen, M. Beller, L. Lefort, E. A. Pidko, *Angew. Chem. Int. Ed.* **2017**, *56*, 7531-7534.
- [10] S. M. Aucott, A. M. Z. Slawin, J. D. Woollins, *J. Chem. Soc., Dalton Trans.* **2000**, 2559-2575.
- [11] D. Benito-Garagorri, K. Mereiter, K. Kirchner, *Collect. Czech. Chem. Commun.* **2007**, *72*, 527-540.
- [12] M. Alvarez, N. Lugan, R. Mathieu, *J. Chem. Soc., Dalton Trans.* **1994**, 2755-2760.
- [13] E. Mothes, S. Sentets, M. A. Luquin, R. Mathieu, N. Lugan, G. Lavigne, *Organometallics* **2008**, *27*, 1193-1206.
- [14] CCDC-1565260-1565263 contains 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.
- [15] a) R. K. Henderson, C. Jimenez-Gonzalez, D. J. C. Constable, S. R. Alston, G. G. A. Inglis, G. Fisher, J. Sherwood, S. P. Binks, A. D. Curzons, *Green Chem.* **2011**, *13*, 854-862; b) S. D. Ramgren, L. Hie, Y. Ye, N. K. Garg, *Org. Lett.* **2013**, *15*, 3950-3953.
- [16] In a competitive experiment, we found that the reduction of acetophenone in the presence of 4-nitrotoluene, was completely inhibited (see Supporting Information Table S3).
- [17] T. Hirata, A. Matsushima, Y. Sato, T. Iwasaki, H. Nomura, T. Watanabe, S. Toyoda, S. Izumi, *J. Mol. Catal. B: Enzym.* **2009**, *59*, 158-162.
- [18] X. Chen, X. Gao, Q. Wu, D. Zhu, *Tetrahedron: Asymmetry* **2012**, *23*, 734-738.
- [19] Mechanistic studies to rationalize the enhancement of activity are under investigations.

COMMUNICATION

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