Received: 10 February 2020 | Revised: 2 March 2020 | Accepted: 4 March 2020

DOI: 10.1002/aoc.5685

FULL PAPER

Applied Organometallic Chemistry WILEY

Sustainable synthesis of quinolines (pyridines) catalyzed by a cheap metal Mn(I)-NN complex catalyst

Huining Chai[1] | **Weiqiang Tan**[1] | **Yuanyuan Lu**[1] | **Guangyao Zhang**[2] | **Jiping Ma**[1]

[1]School of Environmental and Municipal Engineering, Qingdao University of Technology, 11 Fushun Road, Qingdao, 266033, China

[2]Research Center for Intelligent and Wearable Technology, College of Textiles and Clothing, Qingdao University, Qingdao, 266071, China

Correspondence
Huining Chai, School of Environmental and Municipal Engineering, Qingdao University of Technology, 11 Fushun Road, Qingdao 266033, China.
Email: huiningchai@163.com

Guangyao Zhang, Research Center for Intelligent and Wearable Technology, College of Textiles and Clothing, Qingdao University, Qingdao 266071, China.
Email: gyzhang1009@163.com

Funding information
National Natural Science Foundation of China, Grant/Award Number: 21801158; Open Project Fund of Qingdao University of Technology, Grant/Award Number: QUTSEME201934

Abstract

This study represents the first example of a bidentate phosphine-free manganese(I)-NN complex catalyst for the synthesis of quinolines (pyridines) through acceptorless dehydrogenative condensation of various secondary alcohols with amino alcohols. The coupling reactions occurred at 3 mol% catalyst loading and 110°C, and tolerated diverse functional groups. Moderate to excellent yields ranging from 45% to 89% were achieved after 12 hr of reaction. The present protocol provides a concise and environmentally friendly method for the construction of heterocyclic compounds.

KEYWORDS

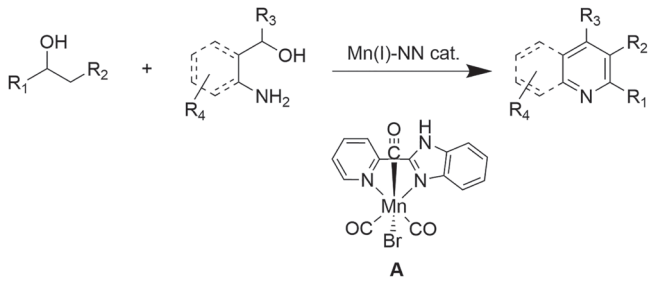
acceptorless dehydrogenative condensation, manganese(I)-NN complex, phosphine-free ligand, quinolines (pyridines)

1 | INTRODUCTION

Quinolines are an important class of nitrogen-containing heterocycles that exist in natural products, drug intermediates, and functional materials.[1–4] Given their importance, the development of new sustainable and one-pot synthetic strategies for the preparation of highly functionalized quinolines is increasingly required. The traditional approach to quinoline synthesis involves the Skraup, Doebner–von Miller, Conrad–Limpach, Pfitzinger, and Friedlaeder methods.[5] However, these methods often suffer from shortcomings such as instability and easy self-condensation of the starting materials and harsh reaction conditions.[6] Recently, transition-metal-catalyzed acceptorless dehydrogenation condensation (ADC) and hydrogen autotransfer (HA) reactions have become useful tools for the construction of heterocyclic compounds due to their atom efficiency and sustainability.[4,7–18] In this regard, direct access to quinolines from abundant and sustainable materials like alcohols is attractive since alcohols are not only available from industrial products but also can be obtained renewably from lignocellulosic biomass.[19,20] Furthermore, only dihydrogen and water are generated as nontoxic byproducts in these transformations. However, the synthesis of quinolines based on ADC reactions mostly uses

less abundant and precious 4d and 5d metal complexes.[21–27] Recently, much attention has been paid to the design of novel complex catalysts based on earth-abundant and nonprecious 3d metals.[28–34] Darcel's group[35] and Zhang's group[36] reported the synthesis of quinoline derivatives by dehydrogenative condensation of ketones with 2-aminobenzyl alcohols using iron and cobalt complex catalysts, respectively. In 2016, Kirchner's group reported the first example of the synthesis of substituted quinolines catalyzed by a hydride Mn(I) PNP complex catalyst through dehydrogenative coupling of secondary alcohols and 2-aminobenzyl alcohols.[37] In 2018, Balaraman *et al.* applied dimeric cobalt complex catalyst to promote the synthesis of quinoline derivatives from secondary alcohols and 2-aminobenzyl alcohols.[38] In 2018, Maji's group and Srimani's group employed trident phosphine-free NNN-manganese and NNS-manganese complexes to synthesize quinoline derivatives, respectively.[39,40] However, stoichiometric amounts of base, excess amounts of secondary alcohols, and high temperature are required. It is therefore necessary to develop a greener and more sustainable catalyst system for these transformations.

Most of the manganese complexes in these ADC/HA reactions possess electron-rich phosphine ligands.[29,37,41–46] Because of the air and moisture sensitivities, toxicity and difficult preparation of phosphine ligands, the exploitation of phosphine-free manganese complexes to catalyze the ADC reactions would be an important advance. Rencently, Yu's group introduced a manganese(I) complex catalyst stabilized by a pyridyl-supported pyrazolyl-imidazolyl ligand, which catalyzes the β-alkylation of secondary alcohols with primary alcohols.[47] In their research, the manganese(I) complex based on the bidentate ligand behaved less selectively and efficiently to the reaction than the tridentate manganese(I) complex. Intrigued by this interesting report and our investigation of cheap metal complex catalysts and green catalytic systems,[48] we began to explore the potential of the simple bidentate phosphine-free Mn(I) complex **A** (Scheme 1) as a precatalyst to prepare quinoline derivatives via ADC reactions of secondary alcohols with 2-aminobenzyl alcohols.



SCHEME 1 Synthesis of quinolines (pyridines) by Mn-NN complex

2 | RESULTS AND DISCUSSION

2.1 | Synthesis and characterization of complex A

The manganese(I) complex catalyst **A** stabilized by a pyridyl-imidazolyl ligand was prepared as depicted in Scheme 2. Reacting equimolar amounts of ligand **L1** and Mn(I) complex $Mn(CO)_5Br$ in methanol at room temperature under a nitrogen atmosphere led to Mn(I)-NN complex **A** in 85% yield. The NMR analyses of the complex are consistent with its composition. In the ^1H NMR spectra, the proton resonances of the NH functionality in ligand **L1** and Mn(I) complex **A** were shown as singlets at 12.90[49] and 14.58 ppm, respectively, suggesting coordination between the metal center and the ligand in the complex. In the ^{13}C NMR spectrum, three singlets appeared at 224.0, 221.0, and 220.6 ppm for the coordinating carbonyl groups in the $Mn(CO)_3$ moiety of complex **A**. Meanwhile, the infrared spectral analysis revealed the absorption peaks of CO functionalities at 2025 and 1937 cm^{-1}, respectively. The solid-state molecular structure of complex **A** was further confirmed by an X-ray crystallographic study (Figure 1, see Supporting Information Data S3 for details). In the solid state, the central manganese atom of complex **A** is situated in a distorted octahedral geometry, coordinated by the pyridyl and imidazolyl nitrogen atoms of ligand **L1** and three CO ligands, and combined to the bromo atom. The bromo ligand is positioned *trans* to one of the carbonyl groups and they are linearly positioned at the two sides of the NN ligand plane with a Br(1)–Mn(1)–N(1,3) angle of 87.2–89.1°, a C(13)–Mn(1)–N(1,3) angle of 92.1–94.5°, and a C(13)–Mn(1)–Br(1) angle of 178.1°. The other two coordinating CO ligands are arranged *trans* to the pyridyl and imidazolyl nitrogen atoms, respectively. The C(14)–Mn(1)–N(1) and C(15)–Mn(1)–N(3) angles are 171.9° and 176.7°, respectively, the Mn–N and Mn–Br bonds are 2.04–2.09 and 2.56 Å, respectively, and the three Mn–C bonds are 1.80–1.82 Å. These results suggest that the Mn atom is situated at the center of a distorted bipyramidal environment.

2.2 | Synthesis of quinolines (pyridines)

The reaction of 1-phenylethanol (**1a**) with (2-aminophenyl)methanol (**2a**) was chosen as a model

SCHEME 2 Synthesis of complex A

Conditions: **L1** (1.0 mmol), $Mn(CO)_5Br$ (1.0 mmol), CH_3OH (25 mL), 0.1 M Pa N_2, 25 °C, 24 h, 85%.

system to optimize the reaction conditions for the acceptorless dehydrogenative coupling to form quinolines. Under a nitrogen atmosphere, treatment of **1a** and **2a** in a 1:1 molar ratio with 3 mol% loading of complex **A** as the catalyst and 0.5 equiv of *t*BuOK as the base in refluxing toluene for 12 hr formed the target product 2-phenylquinoline (**3a**) in 84% yield, as determined by gas chromatography-mass spectrometry (GC-MS) analysis. Subsequently, the base and solvent effects were examined (Table 1, entries 2–7). The reaction experienced significant base effects with in the order *t*BuOK > *t*BuONa > KOH > NaOH. It is noteworthy that in the absence of base *t*BuOK, no product was formed (Table 1, entry 5). Next, different solvents were screened for the reaction and gave decreased yields in the range of 52–61% (Table 1, entries 6–7). Increasing the catalyst loading to 4 mol% did not remarkably improve the product yield (Table 1, entry 8), but further reduction in the catalyst loading decreased the yield of **3a** (Table 1, entry 9). In absence of the catalyst no target product was observed.

Under optimum conditions, the scope of secondary alcohols **1** was explored (Table 2). Various secondary alcohols with functional groups such as methyl, methoxyl, halogen atoms, trifluoromethyl, and long-chain alkyl on the aryl group of 1-arylethanols reacted well with (2-aminophenyl)methanol (**2a**) to form the target quinoline products in good to excellent yields.

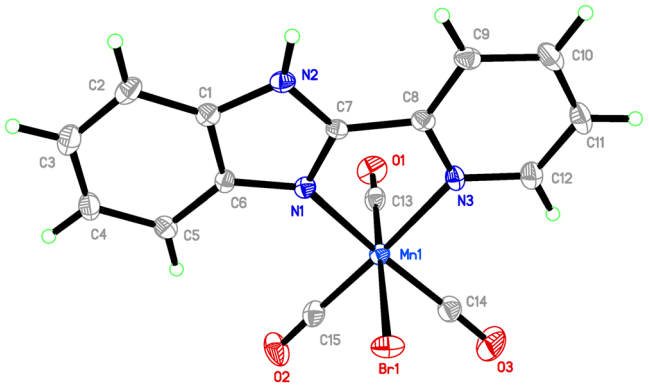
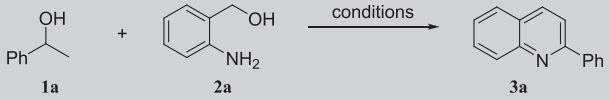


FIGURE 1 Molecular structure of complex **A**

The substituted 1-arylethanols exhibited evident steric effects. *p*-Methyl-substituted 1-phenylethanol reacted efficiently with **2a** to give the corresponding product **3c** in 89% yield, while the *o*-Me-bearing substrate only achieved 63% yield to form the target product **3b**. The *m*- and *p*-OMe substituted 1-phenylethanols showed various reactivities in the formation of **3d**–**3e** (79–83%) and the *m*-OMe substrate reduced the yield of **3d** (79%). The halo-substituted 1-phenylethanols efficiently underwent reaction with **2a**, affording products **3f**–**3h**

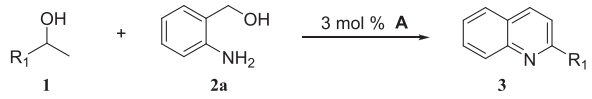
TABLE 1 Screening of reaction conditions[a]

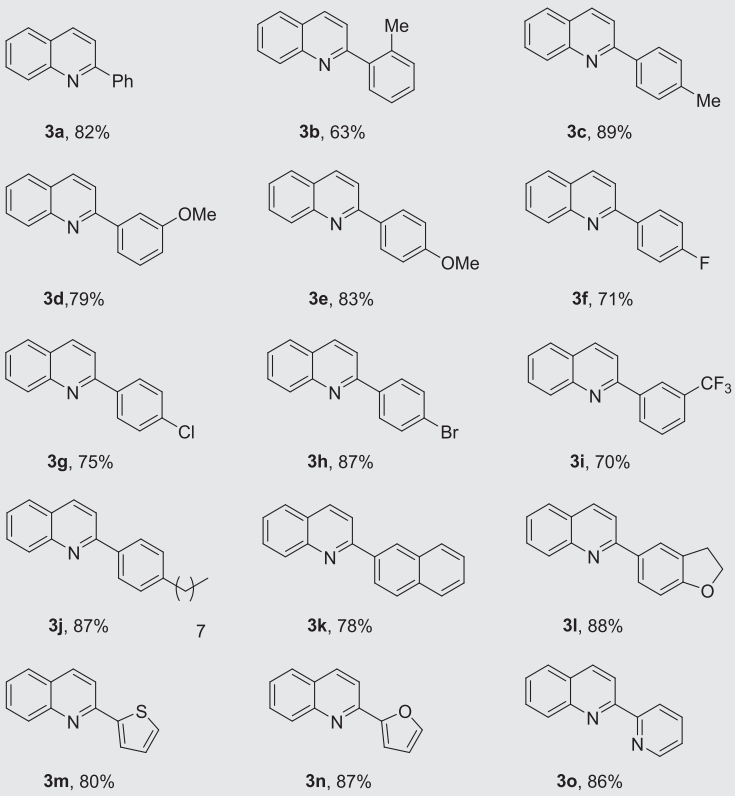


Entry	Catalyst loading (mol%)	Base (0.5 equiv)	Solvent (2 ml)	Yield[b] (%)
1	3	*t*BuOK	Toluene	84
2	3	*t*BuONa	Toluene	74
3	3	NaOH	Toluene	61
4	3	KOH	Toluene	65
5	3		Toluene	0
6	3	*t*BuOK	THF	52
7	3	*t*BuOK	1,4-dioxane	61
8	4	*t*BuOK	Toluene	83
9	2	*t*BuOK	Toluene	75
10	3	*t*BuOK[c]	Toluene	76
11	3	*t*BuOK[d]	Toluene	80
12[e]	3	*t*BuOK	Toluene	67
13[f]	3	*t*BuOK	Toluene	21
14[g]	0	*t*BuOK	Toluene	0

Abbreviation: THF, tetrahydrofuran.
[a]Conditions: **1a** (1 mmol), **2a** (1 mmol), complex catalyst **A** (0.03 mmol), 110°C, 0.1 MPa N_2, 12 hr. [b]Yields determined by GC-MS analysis using *m*-xylene as the internal standard. [c]0.4 equiv *t*BuOK.[d]0.6 equiv *t*BuOK.[e]100°C.[f]Screening in a sealed tube.[g]No catalyst.

TABLE 2 Scope of secondary alcohols **1**[a]



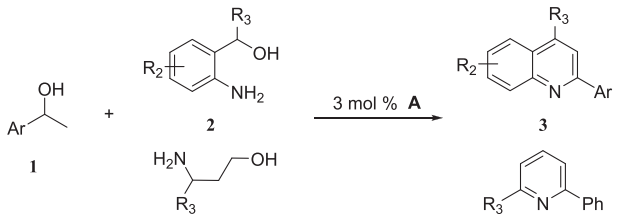


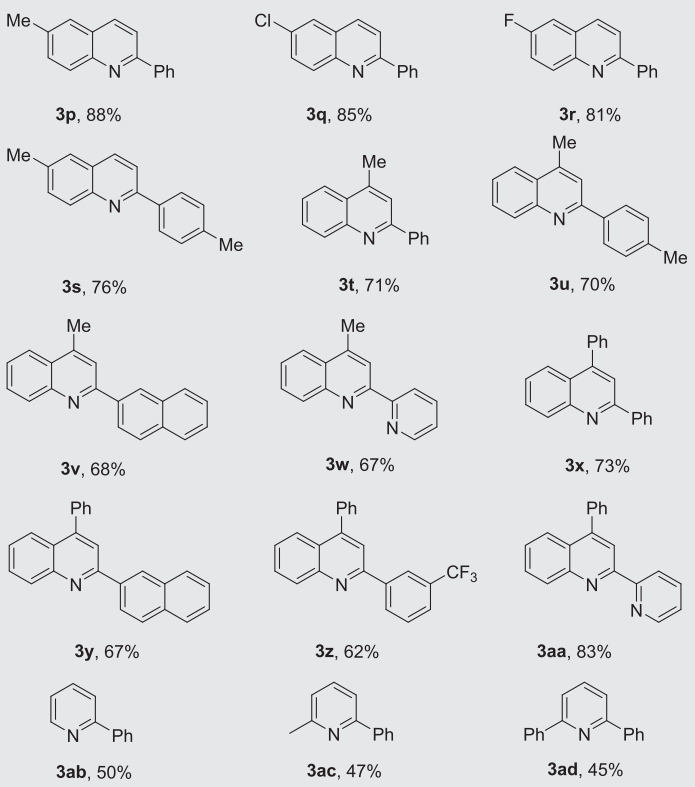
[a]Conditions: **1** (1 mmol), **2** (1 mmol), catalyst **A** (0.03 mmol), *t*BuOK (0.5 mmol), toluene (2 ml), 110°C, 0.1 MPa N_2, 12 hr. Yields refer to the isolated products.

in 71–87% yields in the order 4-F < 4-Cl < 4-Br. The strong electron-withdrawing trifluoromethyl did not demonstrated an obvious negative electronic effect on the yield of **3i** (70%). The 4-octyl moiety of 1-phenylethanol facilitated the formation of **3j** in excellent yield (87%), whereas the bulky 1-(2-naphthyl)ethanol notably reduced the yield of **3k** (70%). The protocol generality was investigated by extending the scope to heteroaromatic substrates. Notably, various heteroaromatic secondary alcohols reacted with **2a** efficiently, giving **3l–3o** in 80–88% yields. It should be noted that higher yields were achieved when using a heteroaromatic substrate, that is, 1-(thiophen-2-yl) ethan-1-ol, 1-(furan-2-yl)ethan-1-ol, and 1-(2-pyridyl) ethanol.

For the scope of reaction to be expanded further, transformations with respect to a variety of substituted 2-amino-benzyl alcohols were conducted (Table 3). Reactions of *o*-aminobenzyl alcohols bearing an electron-donating substituent in a phenyl moiety gave corresponding products **3p** and **3s** in 85% and 76% yields, respectively. Furthermore, *o*-aminobenzyl alcohols bearing an electron-withdrawing substituent (-Cl, -F) were converted to the desired products **3q–3r** in good yields (81–85%). The acceptorless dehydrogenation reaction is not restricted to the primary benzyl alcohols. Both alkyl and aryl substituted secondary 2-aminoaryl alcohols are also efficiently transformed to the corresponding quinolines **3t–3aa** in 62–83% yields. These amino alcohols showed reactivities similar to that of 2-aminobenzyl alcohol as compared to the formation of **3a** (82%), and variation of the substituted moiety in the amino alcohols from methyl to phenyl exhibited no obvious impact on the reaction efficiency.

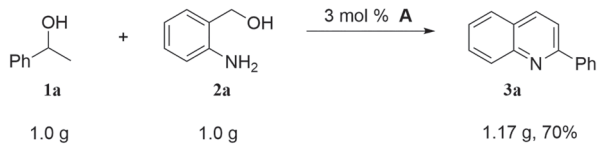
TABLE 3 Scope of amino alcohols **2**[a]





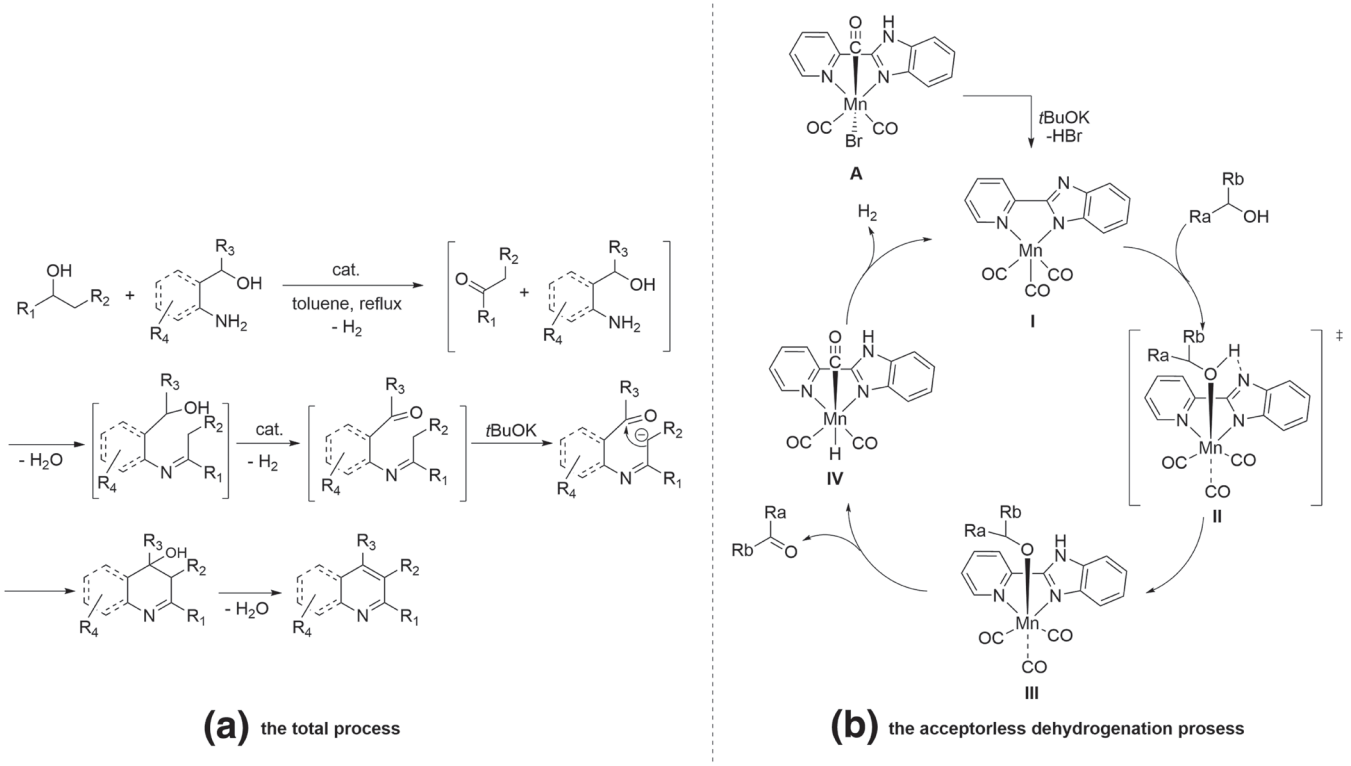
[a]Conditions: **1** (1 mmol), **2** (1 mmol), catalyst **A** (0.03 mmol), *t*BuOK (0.5 mmol), toluene (2 ml), 110°C, 0.1 MPa N_2, 12 hr. Yields refer to the isolated products.

The methyl-functionalized 2-aminobenzyl alcohol also efficiently reacted with sterically hindered or heteroaromatic secondary alcohols to afford products **3v–3w** (67–68%). It should be noted that the reaction of phenyl-substituted 2-aminobenzyl alcohol with bulky 1-(2-naphthyl)ethanol and electron-withdrawing 3-trifluoromethyl substituent 1-phenylethanol generated **3y** (67%) and **3z** (62%), respectively. Meanwhile, the reaction using 1-(pyridin-2-yl)ethan-1-ol gave product **3aa** in 83% yield. In a similar fashion, the reactions of 1-phenylethanol (**1a**) with three different γ-amino alcohols were conducted. Compound **1a** reacted with



SCHEME 3 Gram-scale reaction

Conditions: **1a** (8.19 mmol), **2a** (8.19 mmol), catalyst **A** (0.25 mmol), *t*BuOK (4.09 mmol), toluene (18 mL), 110 °C, 0.1 MPa N_2, 12 h. Yields refer to the isolated products.



SCHEME 4 Proposed mechanism

3-aminopropan-1-ol or 3-aminobutan-1-ol to afford pyridine products **3ab** (50%) and **3ac** (47%), respectively. Phenyl-substituted 3-amino-3-phenyl-propan-1-ol also reacted with **1a** to gain **3ad** (45%). The yields of pyridine products were inferior to those of quinoline compounds.

The catalyst activity was further explored and a gram-scale reaction was carried out under the optimized conditions. Treatment of **1a** (1.0 g**)** and **2a** (1.0 g) in a 1:1 molar ratio formed the target product 2-phenylquinoline (**3a**) in 70% isolated yield (Scheme 3). This protocol offers a potential application for large-scale production of nitrogen heterocyclic compounds.

2.3 | Mechanistic studies

The mechanism proposed for quinoline and pyridine synthesis is shown in Scheme 4. Initially, the acceptorless dehydrogenation of alcohols catalyzed by the manganese(I)-NN complex generates ketones. Subsequent formation of imines is achieved by the condensation of ketones and amines *in situ* and the resulting products can be further coupled in the presence of a base to form quinolines or pyridines (Scheme 4a). In this process, the catalytic dehydrogenation is critical since the acceptorless dehydrogenation of the secondary alcohol catalyzed by the manganese complex generates the corresponding C=O compounds (Scheme 4b). Based on our previous work,[48,50] the process is as follows. First, one equivalent of hydrogen bromide was eliminated in the presence of the base *t*BuOK. Next, the unsaturated 16-electron manganese complex **I** was formed. The reaction intermediate coordinated with alcohol to form complex **III**. Then, the [Mn]-H complex **IV** as well as the C=O compound were formed by β-H elimination of complex **III**. Finally, the H_2 released from the [Mn]-H complex regenerated the 16-electron manganese complex **I** (see Supporting Information Data S2 for details).

3 | CONCLUSIONS

We have developed a sustainable, efficient, and practical synthesis of quinolines (pyridines) catalyzed by a simple bidentate phosphine-free manganese(I)-NN complex through ADC of various secondary alcohols with amino alcohols. Utilization of a complex catalyst based on both a nonprecious metal center and a concise phosphine-free ligand makes this an appealing and meaningful methodology.

4 | EXPERIMENTAL

4.1 | Synthesis of Mn-NN complex

Under a nitrogen atmosphere, a mixture of $Mn(CO)_5Br$ (275 mg, 1.0 mmol) and ligand **L1** (195 mg, 1.0 mmol) in CH_3OH (25 ml) was stirred at 25°C for 24 hr. All the volatiles were removed under reduced pressure, and the resultant residue was subject to purification by recrystallization in $CHCl_2/CH_3OH$/*n*-hexane (1/0.1/3, v/v/v) at 25°C, affording complex **A** as an orange solid (352 mg, 85%). Single crystals suitable for X-ray crystallographic determination were grown from recrystallization in $CHCl_2/CH_3OH$/*n*-hexane (1/0.1/3, v/v/v) at 25°C.

4.2 | General procedure for the synthesis of quinolines (pyridines)

Under a nitrogen atmosphere a mixture of 1-phenylethanol (**1a**) (122 mg, 1.0 mmol), (2-aminophenyl)methanol (**2a**) (123 mg, 1.0 mmol), complex **A** (12.4 mg, 0.03 mmol), and *t*BuOK (56 mg, 0.5 mmol) in 2 ml of toluene was stirred at 110°C for 12 hr. After cooling to ambient temperature, the reaction was quenched with 10 ml of water and extracted with EtOAc (3 × 10 ml). The combined organic phase was concentrated under reduced pressure. The resultant residue was subject to purification by column chromatography on silica gel (eluent: petroleum ether [60–90°C]/ethyl acetate [100:1, v/v]) to afford **3a** as a white solid (168 mg, 82%). About the analytical data and copies of NMR spectra of the compounds, please see the supporting information Data S4, S5 for details.

ACKNOWLEDGMENTS

We are grateful to the National Natural Science Foundation of China (21801158) and the Open Project Fund of Qingdao University of Technology (QUTSEME201934) for support of this research.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

ORCID

Huining Chai https://orcid.org/0000-0001-8087-3458

REFERENCES

[1] S. A. Jenekhe, L. D. Lu, M. M. Alam, *Macromolecules* **2001**, *34*, 7315.
[2] A. Lilienkampf, J. Mao, B. Wan, Y. Wang, S. G. Franzblau, A. P. Kozikowski, *J. Med. Chem.* **2009**, *52*, 2109.
[3] S. Chen, R. Chen, M. He, R. Pang, Z. Tan, M. Yang, *Bioorg. Med. Chem.* **2009**, *17*, 1948.
[4] G. Guillena, D. J. Ramon, M. Yus, *Chem. Rev.* **2010**, *110*, 1611.
[5] G. Jones, in *Comprehensive Heterocyclic Chemistry*, (Eds: A. R. Katritzky, C. W. Rees) Vol. 2, Pergamon, New York **1984** 395.
[6] J. Marco-Contelles, E. Perez-Mayoral, A. Samadi, M. C. Carreiras, E. Soriano, *Chem. Rev.* **2009**, *109*, 2652.
[7] C. Gunanathan, D. Milstein, *Acc. Chem. Res.* **2011**, *44*, 588.
[8] J. Choi, A. H. MacArthur, M. Brookhart, A. S. Goldman, *Chem. Rev.* **2011**, *111*, 1761.
[9] C. Gunanathan, D. Milstein, *Science* **2013**, *341*, 249.
[10] Y. Obora, *ACS Catal.* **2014**, *4*, 3972.
[11] K. I. Shimizu, *Catal. Sci. Technol.* **2015**, *5*, 1412.
[12] Q. Yang, Q. F. Wang, Z. K. Yu, *Chem. Soc. Rev.* **2015**, *44*, 2305.
[13] T. Zell, D. Milstein, *Acc. Chem. Res.* **2015**, *48*, 1979.
[14] A. Quintard, J. Rodriguez, *ChemSusChem* **2016**, *9*, 28.
[15] F. Kallmeier, R. Kempe, *Angew Chem Int Ed* **2018**, *57*, 46.
[16] A. Mukherjee, D. Milstein, *ACS Catal.* **2018**, *8*, 11435.
[17] T. Irrgang, R. Kempe, *Chem. Rev.* **2019**, *119*, 2524.
[18] H. N. Chai, G. Y. Zhang, W. Q. Tan, J. P. Ma, *Appl. Organomet. Chem.* **2020**, *34*, e5367.
[19] T. P. Vispute, H. Zhang, A. Sanna, R. Xiao, G. W. Huber, *Science* **2010**, *330*, 1222.
[20] K. Barta, P. C. Ford, *Acc. Chem. Res.* **2014**, *47*, 1503.
[21] C. S. Cho, B. T. Kim, T. J. Kim, S. C. Shim, *Chem Commun* **2001**, 2576.
[22] H. V. Mierde, P. V. D. Voort, D. D. Vos, F. Verpoort, *Eur. J. Org. Chem.* **1625**, *2008*.
[23] B. W. J. Chen, L. L. Chng, J. Yang, Y. Wei, J. Yang, J. Y. Ying, *ChemCatChem* **2013**, *5*, 277.
[24] B. Pan, B. Liu, E. L. Yue, Q. B. Liu, X. Z. Yang, Z. Wang, W. H. Sun, *ACS Catal.* **2016**, *6*, 1247.
[25] R. Z. Wang, H. J. Fan, W. Zhao, F. Li, *Org. Lett.* **2016**, *18*, 3558.
[26] R. Mamidala, S. Samser, N. Sharma, U. Lourderaj, K. Venkatasubbaiah, *Organometallics* **2017**, *36*, 3343.
[27] M. Maji, K. Chakrabarti, B. Paul, B. C. Roy, S. Kundua, *Adv Synth Catal* **2018**, *360*, 722.
[28] P. Daw, S. Chakraborty, J. A. Garg, Y. Ben-David, D. Milstein, *Angew Chem Int Ed* **2016**, *55*, 14373.
[29] N. Deibl, R. Kempe, *Angew Chem Int Ed* **2017**, *56*, 1663.
[30] F. Kallmeier, B. Dudziec, T. Irrgang, R. Kempe, *Angew Chem Int Ed* **2017**, *56*, 7261.
[31] P. Daw, Y. Ben-David, D. Milstein, *ACS Catal.* **2017**, *7*, 7456.
[32] G. Zhang, S. K. Hanson, *Org. Lett.* **2013**, *15*, 650.
[33] R. Fertig, T. Irrgang, F. Freitag, J. Zander, R. Kempe, *ACS Catal.* **2018**, *8*, 8525.
[34] C. Zhang, B. Hu, D. Chen, H. Xia, *Organometallics* **2019**, *38*, 3218.
[35] S. Elangovan, J. B. Sortais, M. Beller, C. Darcel, *Angew Chem Int Ed* **2015**, *54*, 14483.
[36] G. Zhang, J. Wu, H. Zeng, S. Zhang, Z. Yin, S. Zheng, *Org. Lett.* **2017**, *19*, 1080.
[37] M. Mastalir, M. Glatz, E. Pittenauer, G. Allmaier, K. Kirchner, *J. Am. Chem. Soc.* **2016**, *138*, 15543.
[38] S. P. Midya, V. G. Landge, M. K. Sahoo, J. Rana, E. Balaraman, *Chem Commun* **2018**, *54*, 90.
[39] M. K. Barman, A. Jana, B. Majia, *Adv Synth Catal* **2018**, *360*, 3233.

[40] K. Das, A. Mondal, D. Srimani, *Chem Commun* **2018**, *54*, 10582.
[41] A. Mukherjee, A. Nerush, G. Leitus, L. J. Shimon, Y. Ben-David, N. A. Espinosa-Jalapa, D. Milstein, *J. Am. Chem. Soc.* **2016**, *138*, 4298.
[42] M. Mastalir, M. Glatz, N. Gorgas, B. Stöger, E. Pittenauer, G. Allmaier, L. F. Veirosand, K. Kirchner, *Chem. – Eur. J.* **2016**, *22*, 12316.
[43] S. Chakraborty, U. K. Das, Y. Ben-David, D. Milstein, *J. Am. Chem. Soc.* **2017**, *139*, 11710.
[44] S. Chakraborty, U. Gellrich, Y. Diskin-Posner, G. Leitus, L. Avram, D. Milstein, *Angew Chem Int Ed* **2017**, *56*, 4229.
[45] N. A. Espinosa-Jalapa, A. Kumar, G. Leitus, Y. Diskin-Posner, D. Milstein, *J. Am. Chem. Soc.* **2017**, *139*, 11722.
[46] D. Milstein, A. Kumar, N. A. Espinosa-Jalapa, G. Leitus, Y. Diskin-Posner, L. Avram, *Angew Chem Int Ed* **2017**, *56*, 14992.
[47] T. T. Liu, L. D. Wang, K. K. Wu, Z. K. Yu, *ACS Catal.* **2018**, *8*, 7201.
[48] H. N. Chai, K. Yu, B. Liu, W. Q. Tan, G. Y. Zhang, *Organometallics* **2020**, *39*, 217.
[49] J. S. Casasa, A. Castiñeiras, E. García-Martínez, Y. Parajó, M. L. Pérez-Parallé, A. Sánchez-González, J. Sordo, *Z Anorg Allg Chem* **2005**, *631*, 2258.
[50] H. N. Chai, L. D. Wang, T. T. Liu, Z. K. Yu, *Organometallics* **2017**, *36*, 4936.

SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

How to cite this article: Chai H, Tan W, Lu Y, Zhang G, Ma J. Sustainable synthesis of quinolines (pyridines) catalyzed by a cheap metal Mn(I)-NN complex catalyst. *Appl Organomet Chem*. 2020; e5685. https://doi.org/10.1002/aoc.5685