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FULL PAPER

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Transfer hydrogenation of ketones catalyzed by nickel complexes bearing an NHC [CNN] pincer ligand

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Four NHC [CNN] pincer nickel (II) complexes, [$^{i\mathrm{Pr}}$CNN $(CH_2)_4$-Ni-Br] (**5a**), [$^{n\mathrm{Bu}}$CNN $(CH_2)_4$-Ni-Br] (**5b**), [$^{i\mathrm{Pr}}$CNN $(Me)_2$-Ni-Br] (**6a**) and [$^{n\mathrm{Bu}}$CNN $(Me)_2$-Ni-Br] (**6b**), bearing unsymmetrical [C (carbene)N (amino)N (amine)] ligands were synthesized by the reactions of [CNN] pincer ligand precursors **4** with Ni $(DME)Cl_2$ in the presence of Et_3N. Complexes **5a** and **5b** are new and were completely characterized. The transfer hydrogenation of ketones catalyzed by the four pincer nickel complexes were explored. Complexes **5a** and **6a** have better catalytic activity than **5b** and **6b**. With a combination of NaO^{t}Bu/^{i}PrOH/80 °C and 2% catalyst loading of **5a**, 77–98% yields of aromatic alcohols could be obtained.

KEYWORDS
N-heterocyclic carbene, nickel, pincer complex, transfer hydrogenation

1 | INTRODUCTION

Transfer hydrogenation has been used as an effective substitute method for hydrogenation of ketones not only in heterogeneous catalysis[1] but also in homogeneous catalysis.[2] Because simple alcohols, such as ethanol or *iso*-propanol, are utilized for this transformation as both hydrogen sources and reaction media, transfer hydrogenation has several advantages, such as operational simplicity, easy to access to hydrogen sources, lower cost and good safety.[3,4] The Albrecht group developed Rh (III) complexes bearing C4-bound NHC ligands and found that these Rh complexes could efficiently catalyze transfer hydrogenation of ketones in *iso*-propanol/KOH.[5,6] Nishiyama described that NHC [CCN] pincer Ru complexes were catalytically active for transfer hydrogenation of aromatic ketones.[7] The Yu group prepared a series of [NNN] pincer Ru complexes and investigated their performances as catalysts for transfer hydrogenation of ketones.[8–10] The iron complexes containing macrocyclic ligands were used as catalysts for transfer hydrogenation reactions of aldehydes and keyones.[11–14] High enantioselectivity could be reached using chiral macrocyclic iron complexes as catalysts in the asymmetric transfer hydrogenation of polar double bonds giving high TOF for a broad scope of substrates.[15] We reported the transfer hydrogenation of aldehydes catalyzed by silyl hydrido iron complexes bearing a [PSiP] pincer ligand under mild conditions in moderate to good yields.[16]

In comparison with Rh, Ru and Fe complexes, the study on Ni complexes as homogeneous catalysts for transfer hydrogenation of carbonyl compounds is relatively less. Ojwach and coworkers studied that ((pyrazolyl) ethyl)pyridine Ni (II) complexes could catalyze the transfer hydrogenation of ketones in *iso*-propanol at 82 °C affording conversions of 58–84% within 48 hr.[17] The Whittlesey group discovered low-coordinate NHC Ni(0) complexes used as active catalysts (2 mol%) for transfer hydrogenation of ketones under reflux (> 82 °C) in the presence of NaO^{t}Bu (5 mol%).[18] Ethanol could also be

used as a solvent and a hydrogen donor using Ni(0) complex as a catalyst (2 mol%) for transfer hydrogenation of ketones at 130 °C within 36 hr giving excellent yields.[19]

We found that the NHC [CNN] pincer nickel halides could catalyze the Kumada coupling reactions of aryl chlorides or aryl dichlorides under mild conditions.[20] It has also be confirmed that the related NHC [CNN] pincer nickel hydrides could be used as efficient catalysts for hydrodehalogenation reactions.[21] In this paper we introduced pyrrolidine group, instead of dimethyl amino group, in the NHC [CNN] pincer ligand backbone and synthesized a new kind of [C (carbene)N (amino)N $(CH_2)_4$] pincer ligand precursors. In order to develop more catalytic application of this kind of [CNN] pincer nickel complexes we disclose the performance of [C (carbene)N (amino)N $(Me)_2$] and [C (carbene)N (amino)N $(CH_2)_4$] pincer nickel complexes for transfer hydrogenation of ketones.

2 | RESULTS AND DISCUSSION

2.1 | Syntheses of ligand precursors and [CNN] pincer Ni (II) complexes

The precursor **3** and the [CNN] pincer ligand precursors **4** were prepared by a Pd-catalyzed C, N-coupling reaction according to the literature method (Scheme 1).[20] The reactions of Ni $(DME)Br_2$ with **4a** and **4b** gave rise to [CNN] pincer Ni (II) complexes **5a** and **5b** in the yields of 85 and 90%.

2.2 | Transfer hydrogenation of ketones

The transfer hydrogenation of ketones was studied with complexes **5a**, **5b**, **6a**[20] and **6b**[20] as catalysts (Figure 1). To explore the catalytic activity of complexes **5a – 6b** for transfer hydrogenation, acetophenone was selected as a model substrate to optimize the reaction conditions (Equation (1), Table 1). The control

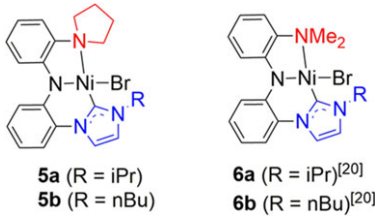
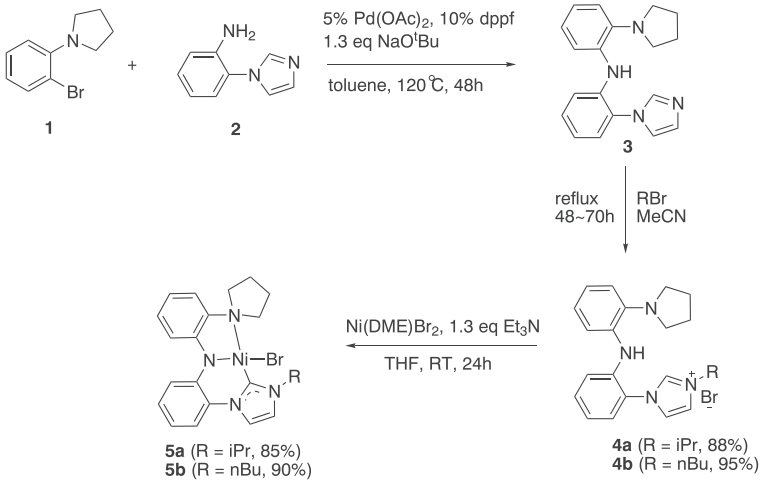


FIGURE 1 [CNN] pincer nickel (II) complexes as catalysts

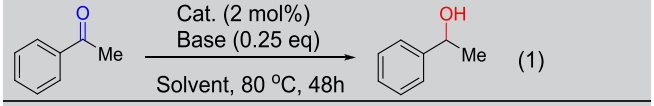
experiments showed that the catalytic reaction did not occur without base (Table 1, Entry 1) or without catalyst (Table 1, Entry 2). **5a** as a catalyst had an excellent performance (GC Yield 99%) under the condition of 2 mol% catalyst loading and 0.25 eq $NaO^tBu/^iPrOH$/80 °C/48 hr (Table 1, Entry 3). Decreasing the amount of NaO^tBu (0.15 eq) or catalyst loading (1 mol%), the yields were correspondingly reduced (Table 1, Entries 4–5). Lower temperature (60 °C) brought the poor yield (Table 1, Entry 6). Different bases were also tested. It was found that the suitable base was NaO^tBu or KO^tBu in comparing to NaO^iPr, NaOH and Cs_2CO_3 (Table 1, Entries 7–10). MeOH and EtOH were adopted for the catalytic system (Table 1, Entries 11–12) but the lower yields of the products were obtained comparing with ^{i}PrOH as solvent. The catalytic behaviors of complexes **6a, 6b, 5a** and **5b** were comparatively investigated for the transfer hydrogenation reactions under the optimized condition. The results showed that the catalytic activity could be ordered in **5a** > **6a** > **5b** > **6b** (Table 1, Entries 3, 13–15). It was considered that the strong electron-donating properties of pyrrolidine and *iso*-propyl group in complex **5a** made the metal center electron-rich. We proposed that one of the intermediate is hydrido nickel complex and its electron-rich property could enhance the activity of Ni-H bond, leading to the best performance. In addition, the steric effect of the isopropyl group in **5a** may play a similar role in comparison with **5b**. However, we cannot confirm whether the electron effect or the steric effect plays a greater role.



SCHEME 1 Synthesis of ligand precursors **4a–4b** and complexes **5a-5b**

Colour online, B&W in print

TABLE 1 Optimization of catalytic reaction conditions



Entry	Cat.	Base	Solvent	Yield [d] (%)
1	**5a**	--	^{i}PrOH	0
2	--	NaO^{t}Bu	^{i}PrOH	0
3	**5a**	NaO^{t}Bu	^{i}PrOH	99
4[a]	**5a**	NaO^{t}Bu	^{i}PrOH	20
5[b]	**5a**	NaO^{t}Bu	^{i}PrOH	60
6[c]	**5a**	NaO^{t}Bu	^{i}PrOH	32
7	**5a**	NaO^{i}Pr	^{i}PrOH	73
8	**5a**	NaOH	^{i}PrOH	10
9	**5a**	KO^{t}Bu	^{i}PrOH	99
10	**5a**	Cs_2CO_3	^{i}PrOH	0
11	**5a**	NaO^{t}Bu	MeOH	15
12	**5a**	NaO^{t}Bu	EtOH	50
13	**5b**	NaO^{t}Bu	^{i}PrOH	88
14	**6a**	NaO^{t}Bu	^{i}PrOH	92
15	**6b**	NaO^{t}Bu	^{i}PrOH	81

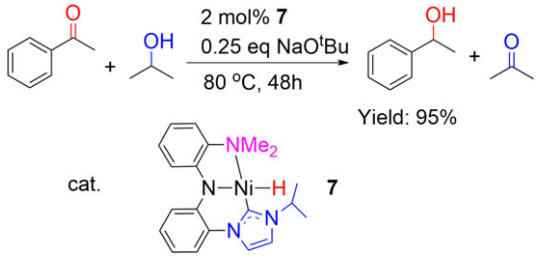
[a]NaO^{t}Bu 0.15 eq;

[b]Cat. loading 1 mol%;

[c]Temperature 60 °C;

[d]GC Yields

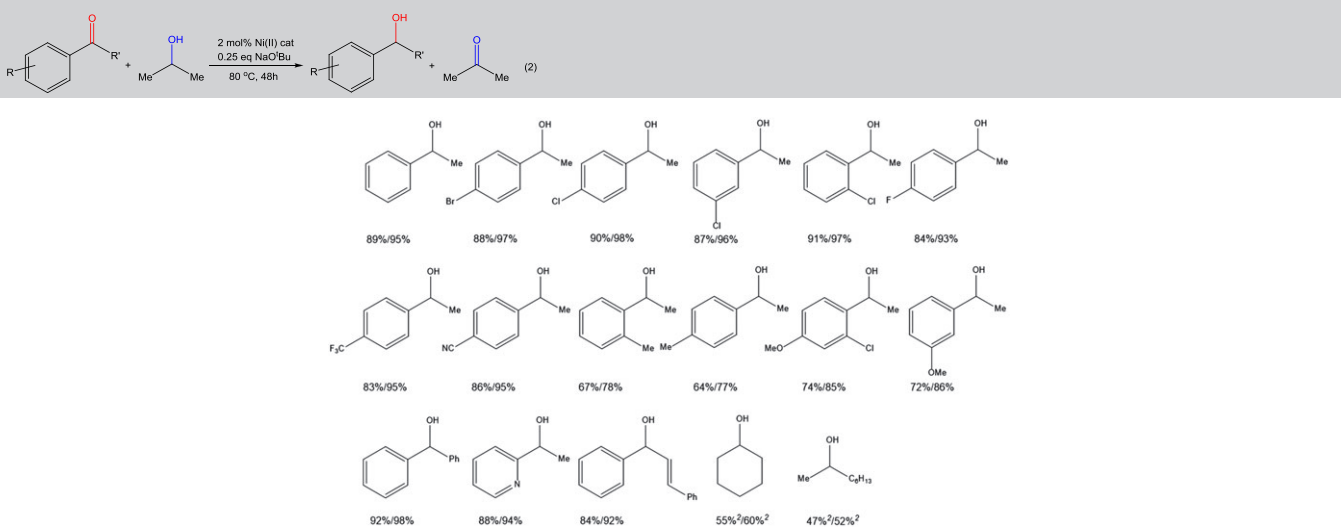
More substrates were selected to study the substituent tolerance and the scope of the substrates under the optimized conditions (Equation (2), **Table** 2). The substrates with the electron-withdrawing groups, such as 4-bromoacetophenone, 4-chloroacetophenone, 3-chloroacetophenone, 2-chloroacetophenone, 4-fluoroacetophenone, 4-trifluoromethylacetophenone and 4-acetylbenzonitrile could be reduced to the corresponding alcohols in excellent yields by using 2 mol% **6a** (84–88%) and 2 mol% **5a** (93–98%) (Table 2, Entries 2–8). For the substrates with the electron-donating groups, moderate yields of the corresponding alcohols could be obtained from this catalytic system (Table 2, Entries 9–12). Benzophenone, 2-acetylpyridine and the α, β-unsaturated compound chalcone were also tolerated in good yields (Table 2, Entries 13–15). Moderate yields could be reached for the aliphatic ketones (Table 2, Entries 16–17). The aromatic ketone substrates containing electron-withdrawing groups were more conducive to the reaction. We consider that the electron-withdrawing groups lead the electrons shifting of the C=O double bond and believe that the electrons shifting is beneficial to the attack on the carbonyl carbon atom by the hydrido atom of the Ni-H bond. The result is that the carbonyl is inserted between Ni-H bond.



SCHEME 2 Transfer hydrogenation catalyzed by **7**

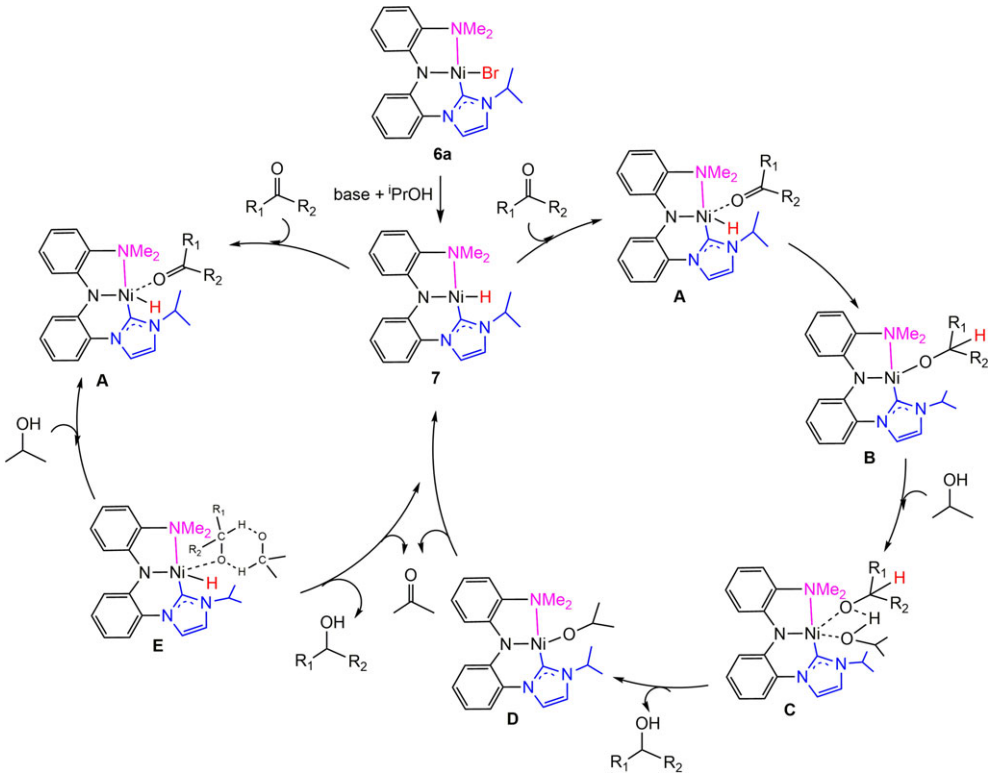
In order to explore the catalytic mechanism, hydrido nickel (II) complex **7**[21] as a catalyst, instead of **6a**, was used for the transfer hydrogenation (TH) of acetophenone under the optimized conditions. We obtained the corresponding product in 95% yield

TABLE 2 Transfer hydrogenation of ketones catalyzed by **5a** and **6a**[a]



[a]Isolated yields;

[b]GC yields. **6a** as catalyst/**5a** as catalyst.



SCHEME 3 Proposed mechanism

(Scheme 2). On the basis of the related report,[10] we proposed that **6a** was catalyst precursor. Nickel (II) hydride **7** as real catalyst is generated *in situ* in the catalytic system (Scheme 3). The coordination of ketones to the nickel atom is the first step to form intermediate **A**. The alkoxy nickel intermediate **B** is produced via the insertion of the carbonyl group into the Ni-H bond. Intermediate **B** reacts with *iso*-propanol to afford intermediate **C** with a four-membered ring. Intermediate **D** is formed with release of the final product alcohol. **D** transfers to **7** with the formation of the byproduct acetone. This is an *Inner sphere* mechanism. However, an *Outer sphere* mechanism is also an alternative. The interaction of **A** with *iso*-propanol gives rise to intermediate **E** with a six-membered ring. **7** is recovered from **E** with the formation of the final product alcohol and the byproduct acetone.

3 | CONCLUSIONS

In summary, four NHC [CNN] pincer nickel (II) complexes, [^{iPr}CNN $(CH_2)_4$-Ni-Br] (**5a**), [^{nBu}CNN $(CH_2)_4$-Ni-Br] (**5b**), [^{iPr}CNN $(Me)_2$-Ni-Br] (**6a**) and [^{nBu}CNN $(Me)_2$-Ni-Br] (**6b**), were synthesized and used as catalysts for transfer hydrogenation reactions of ketones reactions. Strong electron-donating groups on the framework of the pincer ligands could improve the catalytic performance of the nickel complexes for transfer hydrogenation of ketones. Complexes **5a** and **6a** bearing an *iso*-propyl group have better catalytic activity than complexes **5b** and **6b** bearing an *n*-butyl group. With a combination of NaOtBu/iPrOH/80 °C and 2% catalyst loading, 77–98% yields of aromatic alcohols could be formed. The electron-withdrawing groups on ketone substrates were more conducive to the transfer hydrogenation reactions.

4 | EXPERIMENTAL

4.1 | General procedures and materials

All experiments were carried out under N_2 atmosphere and all solvents were freshly distilled before use under an argon atmosphere. Ketones were purchased from commercial sources without purification before use. Infrared spectra (4000 -- 400 cm^{-1}) were recorded on a Bruker ALPHA FT-IR instrument from Nujol mulls between KBr disks. NMR data were obtained on Bruker Avance 300 spectrometer.

4.2 | Synthesis of 3

A 50 ml reaction vessel was charged with Pd $(OAc)_2$ (55.0 mg, 0.25 mmol), bis (diphenylphosphino)ferrocene (DPPF) (0.28 g, 0.5 mmol), NaOtBu (0.65 g, 6.5 mmol) and toluene (15 ml) under a N_2 atmosphere. 2-(1*H*-imidazol-1-yl)phenylamine (0.80 g, 5 mmol) and 1-(2-bromophenyl)pyrrolidine (1.1 g, 5 mmol) were degassed

and added to the reaction mixture. The resulting brown solution was stirred for 48 hours at 120 °C. The solution was then cooled to room temperature and filtered through Celite. Removal of the solvent yielded a purple liquid which was then taken up in 3 ml dichloromethane and was purified through a silica chromatography, dried under vacuum to give **3** (1.03 g, 68% yield) as a brown oil. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K/ppm) δ 7.66 (s, 1H, NC*H*N), 7.33–7.26 (m, 2H, H_{arom}), 7.26–7.19 (m, 3H, H_{arom}), 7.13 (s, 1H, H_{arom}), 7.02–6.95 (m, 2H, H_{arom}), 6.93–6.87 (m, 2H, H_{arom}), 5.87 (s, 1H, N*H*), 3.01–2.93 (m, 4H, NCH_2CH_2CH_2CH_2N), 1.85–1.76 (m, 4H, NCH_2CH_2CH_2CH_2N). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K/ppm): δ 142.4, 140.1, 137.8, 133.3, 130.1, 129.8, 127.4, 123.2, 121.9, 120.3, 120.2, 119.2, 118.3, 115.5, 50.6, 24.3.

4.3 | Synthesis of 4a

To a solution of **3** (3.04 g, 10 mmol) in acetonitrile (30 ml) was added ^{i}PrBr (2.46 g, 20 mmol). The reaction mixture was refluxed for 70 hr. The solution was then cooled to room temperature. After removal of the solvent under vacuum, recrystallization from CH_3OH/Et_2O gave **4a** (3.64 g, 88% yield based on **3**) as a gray powder. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K/ppm) δ: 9.97 (s, 1H, H_{arom}), 7.49 (s, 1H, H_{arom}), 7.37 (d, J = 7.9 Hz, 1H, H_{arom}), 7.30–7.17 (m, 3H, H_{arom}), 6.83–6.97 (m, 5H, H_{arom}), 6.77 (s, 1H, N*H*), 5.08–4.95 (m, 1H, C*H* $(CH_3)_2$), 3.04 (m, 4H, NCH_2CH_2CH_2CH_2N), 1.78 (m, 4H, NCH_2CH_2CH_2CH_2N), 1.50 (d, J = 6.7 Hz, 6H, CH $(CH_3)_2$).^{13}CNMR (75 MHz, $CDCl_3$, 298 K/ppm): δ 139.2, 136.7, 133.6, 131.5, 127.1, 124.5, 124.4, 123.8, 123.2, 121.7, 121.6, 120.4, 120.1, 118.1, 60.4, 53.8, 24.7, 22.5.

4.4 | Synthesis of 4b

To a solution of **3** (3.04 g, 10 mmol) in acetonitrile (30 ml) was added ^{n}BuBr (2.75 g, 20 mmol). The reaction mixture was refluxed for 48 hr. The solution was then cooled to room temperature. After removal of the solvent under vacuum, recrystallization from CH_3OH/Et_2O gave **4b** (3.98 g, 95% yield based on **3**) as a gray powder. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K/ppm): δ 7.67 (s, 1H, H_{arom}), 7.28 (s, 1H, H_{arom}), 7.22 (t, J = 5.0 Hz, 2H, H_{arom}), 7.15–7.05 (m, 3H, H_{arom}), 7.00–6.96 (m, 2H, H_{arom}), 6.95–6.87 (m, 2H, H_{arom}), 6.72–6.45 (m, 2H, CH_2CH_2CH_2), 5.91 (d, J = 20.5 Hz, 1H, N*H*), 2.99 (m, 4H, NCH_2CH_2CH_2CH_2N), 2.79–2.72 (m, 2H, CH_2CH_2CH_2), 2.69–2.62 (m, 2H, CH_2CH_2CH_2), 1.85–1.80 (m, 4H, NCH_2CH_2CH_2CH_2N), 1.76 (t, J = 12 Hz, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K/ppm) δ 139.2, 137.4, 133.1, 131.5, 127.0, 124.2, 123.7, 122.9, 122.8, 122.7, 121.5, 120.2, 117.9, 50.2, 31.9, 24.5, 19.3, 13.5.

4.5 | Synthesis of 5a

A 100 ml reaction vessel was charged with **4a** (1.28 g, 3.0 mmol) and THF (30 ml) under a N_2 atmosphere. Et_3N (0.27 g, 6.6 mmol) was slowly added to the reaction and until the suspension turned to brown solution, Ni (DME) Cl_2 (0.92 g, 3.0 mmol, DME = dimethoxyethane) suspended in THF (10 ml) was added to the solution slowly. The reaction mixture was stirred over night at room temperature. After remove of the solvent under vacuum, the green residue was washed with *n*-pentane (30 ml), then taken up with Et_2O (3 × 20 ml) and filtered through Celite. Evaporation of the solvent yielded a green solid and dried under vacuum. Yield: (1.14 g, 85% based on **4a**). IR (Nujol, cm^{-1}): 1582 ν(C=C). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K/ppm): δ 7.53 (d, J = 8.1 Hz, 1H, H_{arom}), 7.37 (d, J = 1.6 Hz, 1H, H_{arom}), 7.29 (s, 1H, H_{arom}), 7.06 (s, 1H, H_{arom}), 7.05 (d, J = 1.8 Hz, 1H, H_{arom}), 6.98 (t, J = 7.3 Hz, 1H, H_{arom}), 6.89 (dd, J = 15.4, 7.8 Hz, 2H, H_{arom}), 6.73 (t, J = 7.4 Hz, 1H, H_{arom}), 6.55 (t, J = 7.2 Hz, 1H, H_{arom}), 5.76–5.67 (m, 1H, C*H* $(CH_3)_2$), 4.17–4.01 (m, 1H, NCH_2CH_2CH_2CH_2N), 3.94–3.85 (m, 1H, NCH_2CH_2 CH_2CH_2N), 3.45–3.32 (m, 1H, NCH_2CH_2CH_2CH_2N), 3.06–3.00 (m, 3 Hz, 1H, NCH_2CH_2CH_2CH_2N), 2.14–2.03 (m, 1H, NCH_2CH_2CH_2CH_2N), 1.97–1.85 (m, 1H, NCH_2CH_2CH_2CH_2N), 1.84–1.73 (m, 2H, NCH_2CH_2 CH_2CH_2N), 1.69 (d, J = 6.8 Hz, 3H, C $(CH_3)_2$), 1.42 (d, J = 6.6 Hz, 3H, C $(CH_3)_2$). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K/ppm): δ 150.3 ($C_{carbene}$), 149.9, 145.8, 142.5, 130.6, 126.5, 126.2, 121.5, 120.4, 119.7, 119.5, 118.0, 117.4, 117.1, 115.8, 60.4, 54.5, 51.2, 25.3, 24.5, 23.3, 22.4. Anal. Calcd for $C_{22}H_{25}BrN_4Ni$ (%): C, 54.59; H, 5.21; N, 11.57. Found (%): C, 54.01; H, 5.50; N, 11.30.

4.6 | Synthesis of 5b

A 100 ml reaction vessel was charged with **4b** (1.32 g, 3.0 mmol) and THF (30 ml) under a N_2 atmosphere. Et_3N (0.27 g, 6.6 mmol) was slowly added to the reaction and until the suspension turned to brown solution, Ni (DME)Cl_2 (0.92 g, 3.0 mmol) suspended in THF (10 ml) was added to the solution slowly. The reaction mixture was stirred over night at room temperature. After remove of the solvent under vacuum, the green residue was washed with *n*-pentane (30 ml), then taken up with Et_2O (3 × 20 ml) and filtered through Celite. Evaporation of the solvent yielded a green solid and dried under vacuum. Yield: (1.22 g, 90% based on **4b**). IR (Nujol, cm^{-1}): 1582 ν(C=C). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K/ppm): δ 7.48 (dd, J = 8.4, 1.0 Hz, 1H,

H_{arom}), 7.26 (d, J = 2.0 Hz, 1H, H_{arom}), 7.21 (d, J = 1.4 Hz, 1H, H_{arom}), 6.98 (dd, J = 8.1, 1.2 Hz, 1H, H_{arom}), 6.93 (d, J = 7.5, 1.2 Hz, 1H, H_{arom}), 6.90 (d, J = 2.1 Hz, 1H, H_{arom}), 6.85–6.76 (m, 2H, H_{arom}), 6.69–6.62 (m, 1H, H_{arom}), 6.50–6.44 (m, 1H, H_{arom}), 4.64 (m, 1H, $CH_2CH_2CH_2$), 4.22 (m, 1H, $CH_2CH_2CH_2$), 4.11–4.01 (m, 1H, m, 1H, $NCH_2CH_2CH_2CH_2N$), 3.88–3.78 (m, 1H, $NCH_2CH_2CH_2CH_2N$), 3.36–3.25 (m, 1H, $NCH_2CH_2CH_2CH_2CH_2N$), 2.98–2.91 (m, 1H, $NCH_2CH_2CH_2CH_2N$), 2.22–2.10 (m, 1H, $NCH_2CH_2CH_2CH_2N$), 2.06–1.99 (m, 1H, $NCH_2CH_2CH_2CH_2N$), 1.78–1.69 (m, 2H, $NCH_2CH_2CH_2CH_2N$), 1.58–1.45 (m, 2H, $CH_2CH_2CH_2$), 1.20–1.14 (m, 2H, $CH_2CH_2CH_2$), 1.01 (t, J = 7.4 Hz, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K/ppm): δ 149.4 ($C_{carbene}$), 148.9, 145.8, 141.6, 129.6, 125.6, 125.3, 122.7, 120.5, 119.3, 118.6, 117.0, 116.4, 115.9, 114.8, 59.6, 54.2, 49.5, 32.6, 28.7, 24.4, 18.9, 12.9. Anal. Calcd for $C_{23}H_{27}BrN_4Ni$ (%): C, 55.46; H, 5.46; N, 11.25. Found (%): C, 55.03; H, 5.71; N, 11.45.

4.7 | Typical procedure for the catalytic transfer hydrogenation of ketones

The catalyst solution was prepared by dissolving complex **5a** (0.439 g, 1 mmol) in 2-propanol (50.0 mL). Under a nitrogen atmosphere, a mixture of a ketone (1.0 mmol), NaO^tBu (24.5 mg, 0.25 mmol), 1.0 ml of the catalyst solution (0.02 mmol), and 2-propanol (5 ml) was stirred at 80 °C for 48 hr. Then the reaction solution was cooled to the room temperature and quenched with 15 ml of water. After extraction with Et_2O (3 × 20 ml), the extraction solution was dried over Na_2SO_4. The catalytic product could be obtained by flash chromatography on silica gel.

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CONFLICT OF INTEREST

There are no conflicts to declare.

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SUPPORTING INFORMATION

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

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