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Ruthenium Pincer-Catalyzed Hydrogenation of Lactams to Aminoalcohols

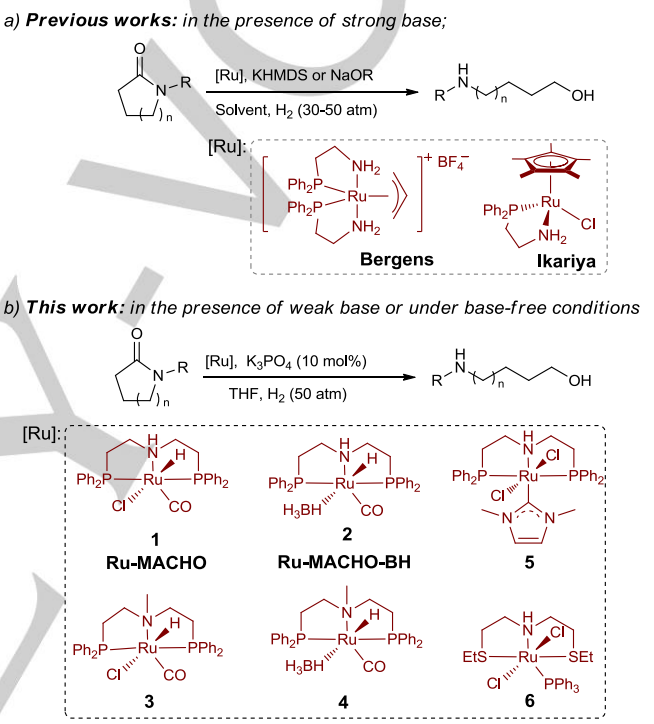
Jiangbo Chen,[a] Jiaquan Wang[a] and Tao Tu*[a, b]

Abstract: By using commercial available ruthenium pincer complex (Ru-MACHO-BH) as a catalyst, the challenging direct hydrogenation of lactams and analogues has been accomplished to successfully deliver corresponding value-added aminoalcohols in good to excellent yields under mild reaction conditions. Remarkably, besides N-protected lactams, unprotected ones could also be readily reduced in the presence of a catalytic amount of weak base or even under neutral reaction conditions, further highlighting broad substrate scopes and the protocol efficiency.

Introduction

As one of the most important building blocks extensively utilized for the producing of pharmaceutical compounds,[1] for the fabrication of auxiliaries[2] or catalysts in various catalytic transformations,[3] and for biologic materials syntheses and assembly,[4] aminoalcohols have drawn considerable attention from diverse research fields.[5] In the past decades, a number of protocols have been successfully developed for the synthesis of diverse aminoalcohols, including transition-metal catalyzed aminohydroxylation of olefins,[6] ring opening nucleophilic amination of epoxides[7] and so on.[8] However, multi-step and tedious operation precedures are usually required under the harsh reaction conditions in these synthetic protocols, which hampered their practical applications.

Direct hydrogenation of amino acids, esters and lactams is considered as another efficient and much straightforward approach to access a variety of aminoalcohols.[8] Unlike the conventional reduction usually carried out with stoichiometric amounts of hydride reagents and generated stoichiometric waste, catalytic hydrogenation using molecular H_2 constitute a much more attractive and atom-economical approach. To the best of our knowledge, among them, only two examples of direct hydrogenation of lactams were reported by Ikariya and Bergens (scheme 1a).[9] Due to the low electrophilicity of the carbonyl group of lactam, the reductive cleavage of inert C-N with H_2 is considered as a very challenging task and usually occurs at elevated pressures, high reaction temperatures with extended reaction time in the presence of strong bases (usually potassium *tert*-butoxide[9c] or potassium hexamethyl disilazane[9a]). From an environmental point of view, it would be practical and convenient to produce aminoalcohols under neutral or at least weak alkali reaction conditions.



Scheme 1. Ru-catalyzed hydrogenation of lactams with a) strong, b) weak bases or under the base-free reaction conditions.

Recently, a number of catalytic systems have been demonstrated ruthenium pincer complexes could be functioned as privileged catalysts in the direct hydrogenation of linear amides for corresponding amines and primary alcohols syntheses.[10-13] Under the mild reaction conditions, ruthenium pincer complex **1** (Ru-MACHO, Scheme 1), a commercial available bifunctional catalyst, has exhibited extremely high catalytic activity in hydrogenation of ketones, amides or carboxyl esters in the presence of suitable strong base.[14] In contrast, it's hydride analogue **2** (Ru-MACHO-BH, Scheme 1b) does not require a strong base for its activation in the similar hydrogenation reactions, due to the lack of chloride ligand.[15] In consideration that the N-H group and Ru-H moiety of pincer complex **1** were all essential for the activation of the challenging amide C-N bond,[9a] N-methylated pincer complexes **3** and **4** were also reported as privileged catalysts in the hydrogenation of carbon dioxide.[16] In addition, the catalytic activity of Ru-pincer complexes is also strongly affected by the electron density of ruthenium center in the hydrogenation reactions.[17] By using N-hetercyclic carbene (NHCs, strong σ-donors and weak

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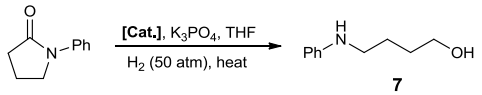
π-acceptors) or thiol-esters to replace phosphines, complexes **5** and **6** were therefore reported and also exhibited high catalytic activity in the hydrogenation of ketones, esters or olefins.[18,19] However, to the best of our knowledge, their catalytc activities for all these six Ru-pincer complexes in the hydrogenation of lactams are still unknown. Following our recent interests in the pincer complexes and their application in catalysis and material sciences,[20] herein, we would like to explore their catalytic activities of Ru-pincer complexes in the direct hydrogenation of lactams to access diverse aminoalcohols, especially, in the presence of weak base or even under neutral reaction conditions.

Results and Discussion

Table 1. Optimization of hydrogenation reaction conditions. [a]

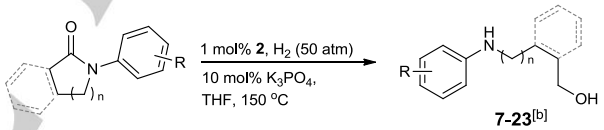


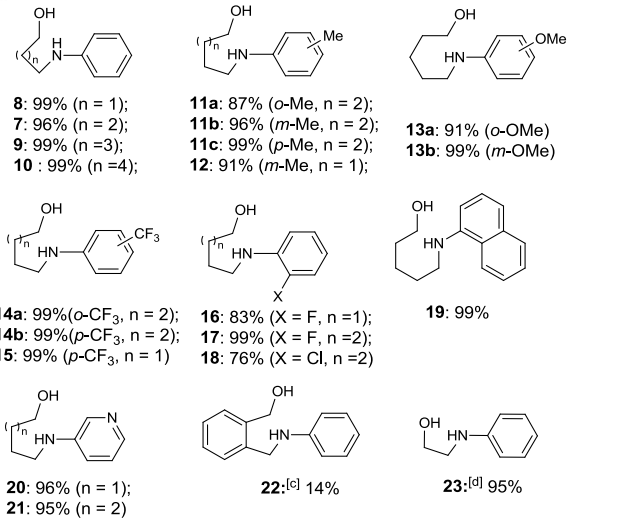
Entry	[Cat.]	Base	Temp. (°C)	Yield (%)[b]
1	**1**	/	140	trace
2	**2**	/	140	53
3	**2**	K_3PO_4	140	89
4	**2**	Na_3PO_4	140	58
5	**2**	KF	140	68
6	**2**	KPF_6	140	20
7	**2**	K_2CO_3	140	trace
8	**2**	K_2HPO_4	140	75
9	**2**	KH_2PO_4	140	82
10	**2**	KO*t*Bu	140	86
11	**2**	KOH	140	81
12	**2**	/	150	64
13	**2**	K_3PO_4	150	96
14	**3**	K_3PO_4	150	trace
15	**4**	K_3PO_4	150	trace
16	**5**	K_3PO_4	150	82
17	**6**	K_3PO_4	150	37

[a] Reaction was carried out under 50 atm H_2 pressure with 0.5 mmol N-phenyl-2-pyrrolidone in 2 mL THF and 10 mol% base in the presence of 1 mol% Ru-pincer complex at 140 °C for 24h; [b] Yield was determined by NMR analysis by using 1,3-Dimethoxybenzene as an internal standard.

In consideration that there are two possible resonance structures for amides,[21] only the –C=N– resonance structure could conjugate with the phenyl π-ring, which be favor for the challenging reductive cleavage of inert amide C-N bond,[9b] N-phenyl-2-pyrrolidone was initially selected as a substrate to investigate the catalytic activities of Ru-pincer complexes of **1-6** in the hydrogenation of lactams. The reaction was carried out in THF under 50 atm H_2 pressure at 140 °C for 24 hours. No reaction occurred when 1 mol% Ru-MACHO **1** was applied under base-free conditions (Table 1, entry 1). In contrast, when it's hydride analogue **2** (1 mol% Ru-MACHO-BH) was utilized instead, a moderate yield was presented for the aminoalcohol **7** under the identical reaction conditions (53%, Table 1, entry 2). A catalytic amount of weak base is benefit for the hydrogenation transformation, a good yield for product **7** was observed when 10 mol% K_3PO_4 was added (89%, Table 1, entry 2). When other weak bases including Na_3PO_4, KF, KPF_6 and K_2CO_3 were applied under the identical reaction conditions, no better results were presented (<68%, Table 1, entries 4-7). To our delighted, good yields were still observed even with salts like K_2HPO_4 and KH_2PO_4 (75% and 82%, respectively, Table 1, entries 8 and 9). In consideration strong bases always resulted in better outcomes in the previous studies,[9] 10 mol% KO*t*Bu and KOH were then selected as bases in the hydrogenation. However, good but lower yields than what observed with K_3PO_4 were provided under the identical reaction conditions (86%, 81% vs 89%, Table 1, entries 10 and 11 vs. 3). The temperature affected the hydrogenation outcomes. When the reaction temperature was increased to 150 °C, 64% and 96% yields could be obtained without and with 10 mol% K_3PO_4, respectively (Table 1, entries 12 and 13). No better results were found with other selected solvents and organic bases even with extended reaction times (see the Supporting Information).

Table 2. Substrate scopes of N-aryl lactams and their analogues. [a]



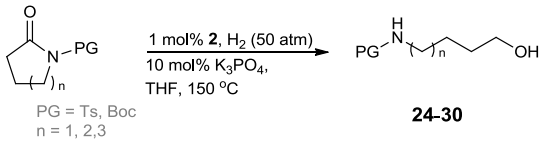


[a] Reaction was carried out under 50 atm H_2 pressure with 0.5 mmol lactam in 2 mL THF and 10 mol% K_3PO_4 in the presence of 1 mol% Ru-pincer **2** at 150 °C for 24h; [b] Yields were determined by NMR analysis; [c] Hydrogenated from 2-phenylisoindolin-1-one; [d] Hydrogenated from 3-phenyloxazolidin-2-one.

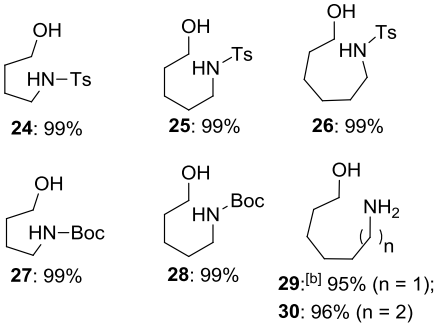
With the optimized reaction conditions in hand, the catalytic activities of other Ru-pincer complexes **3**-**6** in the model reaction

were then evaluated. When N-methylated Ru-pincer complexes **3** and **4** were used under the otherwise identical reaction conditions, almost no products were detected, further indicating the importance role of N-H moiety during the catalytic cycle (Table 1, entries 14 and 15). Although NHC ligands can increase the electron density of ruthenium center and accelerate the heterolysis of H_2 molecular, no better yield was presented compared with complex **2** under the standard reaction conditions (82% vs 96%, Table 1, entries 16 vs. 13). SNS-Ru pincer **6** only exhibited very low catalytic activity towards the hydrogenation of N-phenyl-2-pyrrolidone, probably due to the absence of Ru-H moiety (37%, Table 1, entry 17).

Table 3. Scope of (hetero)aryl alkynes. [a]

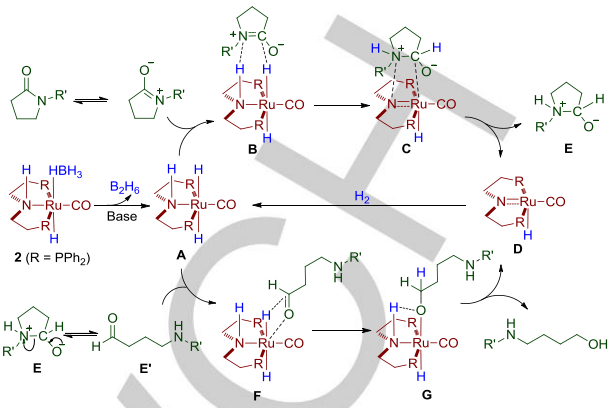


24-30



[a] Reaction was carried out with 0.5 mmol lactam in 2 mL THF and 10 mol% K_3PO_4 in the presence of 1 mol % **2** at 150 °C for 24hrs; [b] Yield of product was determined by NMR analysis; [c] 2 mol% **2** with 20 mol% K_3PO_4.

Subsequently, the substrate scope of the established protocol was then evaluated under the optimized reaction conditions (Table 2). At first, N-phenyl substituted lactams with different ring sizes were involved. As our expected, the propiolactam, valerolactam and caprolactam derivatives were all successfully reduced and produced the corresponding aminoalcohols **8**-**10** in almost quantitative yields, indicating the feasibility of the protocol. Furthermore, the electron-properties of substituents on the N-phenyl ring hardly show any effect on the reductive transformation; good to excellent yields were provided (**11**-**15**). It has to be pointed out the position of substituent on the N-phenyl ring show slightly impact on the outcomes: *ortho*-, *meta*- and *para*- methyl substitutes all resulted in good to excellent yields (87%, 96% and 99% for **11a**, **11b**, and **11c**, respectively). Gratifyingly, the halide groups were also fully compatible (76%-99%, **16**-**18**), whereas, and the ring-size of lactams shows slightly impacts on the yields. To our delight, sterically hindered N-naphthalen-1-yl-2-pyrrolidone also resulted in a quantitative yield (**19**). In the case of lactams with N-heterocyclic aromatic groups, the hydrogenation also processed very well and excellent yields were still observed (**20** and **21**), although pyridine moiety has strong coordination ability to Ru center. Pleasingly, the protocol is also compatible with isoindolinone and oxazolidinone, 14% and 95% yields were obtained when N-phenyl-isoindolin-1-one and N-phenyl-oxazolidin-2-one were applied under the standard reaction conditions.



Scheme 2. Plausible mechanism of catalytic hydrogenation of lactams.

In order to access unprotected aminoalcohols, other lactams containing readily deprotected groups including toluene sulfonyl (Ts) and *tert*-butyloxycarbonyl (Boc) were then involved under the standard reaction conditions. To our delight, lactams containing Ts and Boc groups all led to quantetative results with different ring size. (**24**-**28**). Furthermore, after a simple deprotection step (usually acid hydrolysis), free aminoalcohols could be produced in excellent yields, which demonstrated the great applicability of this protocol. With this good outcome in hand, we would like to investigate the feasibility of our protocol for the direct hydrogenation of unprotected lactams, which is considered as extremely challenging issues in this field.[9] Unlike only low or even no reaction occurring in the previous study with strong bases,[9a] azepan-2-one and azocan-2-one were readily reduced by our catalytic system to generate corresponding aminoalcohols **29** and **30** in 95% and 96% yields, respectively, further highlighting our protocol efficiency. It has to be pointed out that the reduction of azepan-2-one with small ring is more challenging, 2 mol% catalyst loading was required to achieve the excellent yield.

With all these exciting outcomes in hand, a plausible mechanism of the catalytic hydrogenation of diverse lactams in the presence of Ru-MACHO-BH complex **2** was proposed in Scheme 2. Initially, the *cis*-dihydride species **A** was generated from complex **2** after B_2H_6 liberation, which may act as the actual catalyst in the subsequent hydrogenation transformations.[5a] It has to be pointed out that catalytic amount of weak base may facilate the B_2H_6 liberation. The cationic contributor of pyrrolidone resonance structures was readily approaching to species **A** leading to adduct **B** formation. After direct hydrides transformation from Ru-H and N-H to C=N double bond via the "outer-sphere" route,[10] intermediate **C** was formed, which might further undergo a crucial elimination step to generate pincer intermediate **D** along with key saturated cyclic intermediate **E** formation. The active species **A** was readily regenerated from **D** after hydrogen addition, which could further coordinate to the aminoaldehyde **E'**, an isomer of cyclic intermediate **E**, leading to the intermediate **F** formation. After the insertion of Ru-H and N-H to C=O double bond, inactive intermediate **D** could be regenerated from **G** after elimination to complete the catalytic cycle, along with the product aminoalcohol formation.

Conclusions

In summary, by using commercial available Ru-MACHO-BH as a catalyst, the challenging hydrogenation of lactams has been accomplished under relatively mild reaction conditions to deliver a variety of aminoalcohols in good to excellent yields. Besides a number of N-protected lactams and their analogues, even extremely challenging unprotected cyclic amides were readily reduced to generate corresponding unprotected aminoalcohols in excellent yields, further highlighting the protocol efficiency. Unlike previous studies with strong bases, all these transformations processed efficiently only in the presence of a catalytic amount of K_3PO_4. Remarkably, in some cases, products could be obtained even under base-free conditions, indicating their applicability. In combination of our outcomes with previous reports, a plausible mechanism was therefore proposed.

Experimental Section

General: All commercial reagents were used directly without further purification, unless otherwise stated. Dry dimethylsulfoxide (DMSO) and *N,N*-Dimethylformamide (DMF) were purchased from *J & K* chemical, stored over 4 Å molecular sieves and handled under N_2. Anhydrous methanol (MeOH) was distilled from anhydrous calcium chloride, Dioxane, Tetrahydrofuran (THF) and toluene were distilled from sodium/benzophenone, 1,2-Dichloroethane (DCE) was distilled from calcium hydride prior to use. K*t*OBu was purchased from J & K chemical. All Schlenk tubes and sealed vessels (50 mL) were purchased from Beijing Synthware Glass. $CDCl_3$ was purchased from Cambridge Isotope Laboratories. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on Jeol ECA-400 and Bruker 400 DRX spectrometers. ^{13}C NMR spectra were referenced to the carbon signal of $CDCl_3$ (77.0 ppm).

Synthesis of Ru-pincer complexes 1-6.

Ru-pincer complex 1:[17] To a 100 mL Schlenk tube were added $HCl{\cdot}HN(CH_2CH_2PPh_2)_2$ (1.20 g, 2.51 mmol), toluene (20 mL), and 15% aqueous NaOH solution (10 mL) under an N_2 atmosphere. The resulting mixture was stirred at room temperature until the solid disappeared. After phase separation, the organic layer was washed twice with distilled water (5 mL), and the combined aqueous layer was extracted twice with toluene (2 ×10 mL). The combined organic phase was dried over anhydrous Na_2SO_4, filtered, and the solvent was removed under vacuum to afford the crude amine product $HN(CH_2CH_2PPh_2)_2$ as a thick yellowish oil. The crude amine, without further purification, was dissolved in toluene (18 mL), followed by addition of $RuHCl(CO)(PPh_3)_3$ (2.28 g, 2.39 mmol) under an N_2 atmosphere. The resultant mixture was heated to reflux for 2 h. After being cooled to rt, the solution was diluted with hexane (10 mL), and the precipitate was filtered. The pale yellow solid thus obtained was washed with hexane (5 mL), then dried under vacuum. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.82-7.71 (m, 8H), 7.51-7.16 (m, 12H), 4.35 (brs, 1H), 3.39-3.26 (m, 2H), 2.81-2.76 (m, 2H), 2.44-2.35 (m, 4H), -15.41 (t, *J* = 19.6 Hz, 1H).

Ru-pincer complex 2:[22] Ru-MACHO catalyst (0.5 mmol) was suspended in 50 mL/50 mL of toluene/ethanol. Thereafter, $NaBH_4$ (13.5 mmol) was added to the suspension and stirred for 30 minutes at 70 °C. Then the mixture was cooled to room temperature and keeps stirring overnight. The solvent was removed under reduced pressure. 50 mL of dichloride methane and 25 mL of distilled water were added, stirred for 15 min. The organic phase was dried over anhydrous Na_2SO_4 and filtrated. The solvent was concentrated to 10 mL followed by addition of hexane to afford the desired Ru-MACHO-BH complex. ^{1}H NMR (400MHz $CDCl_3$): δ = 7.70-7.82 (m,8H), 7.38-7.46 (m,12H), 4.20-4.40 (m,1H), 3.32-3.60 (m,2H), 2.90-3.05 (m, 2H), 2.40-2.78 (m, 4H), -2.80-1.70 (brs, 4H), -12.36 (t, *J* = 28.5 Hz, 1H).

Ru-pincer complex 3:[18] To a 50 mL round-bottomed flask were added $HCl{\cdot}HN(CH_2CH_2PPh_2)_2$ (724 mg, 1.51 mmol), 15% NaOH aqueous (10 mL), and toluene (10 mL). The mixture was stirred at room temperature until the solids dissolved. After separation of the solution, the organic layer was washed with H_2O (5 mL × 2), dried over Na_2SO_4, and then concentrated under reduced pressure. The resulting PNP was diluted with 3 mL of ethanol. To a 20 mL Schlenk flask were added $RuCl_2$(p-cymene)(NHC) (609.3 mg, 1.51 mmol) and the PNP solution under a nitrogen atmosphere. The reaction mixture was stirred at 70 °C for 2 hours, and then cooled to room temperature. After removal of ethanol under reduced pressure, 3 mL of hexane was added to the mixture. The resulting precipitates were separated by filtration, washed with hexane (2 mL × 2) and ethyl acetate (2 mL), and then dried under reduced pressure to give 3 as a pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.20-7.50 (m, 20H), 6.78-6.86 (m, 2H), 4.20-4.40 (m, 1H), 3.19-3.50 (m, 4H), 3.21 (s, 3H), 3.07 (s, 3H), 2.95-3.15 (m, 2H), 2.60-2.80 (m, 2H).

Ru-pincer complex 4:[17] A mixture of $CH_3N(CH_2CH_2PPh_2)_2$ (217 mg, 0.710 mmol) and $RuHCl(CO)(PPh_3)_3$ (644 mg, 0.676 mmol) in degassed toluene (4 mL) was heated to reflux for 5 h. After being cooled to room temperature, the mixture was diluted with hexane (6 mL). The resulting pale yellow solid was collected by filtration and then dried under vacuum. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.85-7.60 (m, 8H), 7.45-6.76 (m, 12H), 3.37-3.50 (m, 2H), 2.95-2.91 (m, 2H), 2.74-2.66 (m, 2H), 2.55-2.46 (m, 2H), 2.35 (s, 3H), -14.46 (t, *J* = 19.6 Hz, 1H).

Ru-pincer complex 5:[22] The procedure of preparation of BH_4 containing **5** was accorrding to the preparation of complex **2**. ^{1}H NMR (400MHz $CDCl_3$): δ =, 7.70-7.82 (m,8H), 7.38-7.46 (m,12H), 3.38-3.55 (m,2H), 2.65-3.00 (m, 2H), 2.51 (s, 3H), 2.20-2.58 (m, 4H), -2.50-1.65 (brs, 4H), -12.16 (t, *J* = 28.5 Hz, 1H).

Ru-pincer complex 6:[19] A 100 mL Schlenk flask containing a mixture of $RuCl_2(PPh_3)_3$ (15.00 g, 15.66 mmol) and $(EtSC_2H_4)_2NH$ (3.03 g, 15.7 mmol) in 50 mL of toluene was heated at 100 °C for 2 h to get a yellow suspension. The product was filtered in air, washed with 35 mL of Et_2O to give a yellow solid which was dried under vacuum for 2 h.

General procedure for the synthesis of N-protected lactam: N-phenyl lactam: Under an atmosphere of nitrogen, aryl iodide (2 mmol, 1 eq.) was added to the mixture of amide (2 eq.),

K_3PO_4 (2 eq.), and CuI (10 mol%) in DMSO (3 mL) at r.t. The mixture was stirred at 110 °C in dark. After 24 h, the mixture was cooled to r.t, diluted with H_2O, then extracted with EtOAc for three times. The combined organic phase was dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure, and the resulting residue was purified by silica gel chromatography using a mixture of hexane and EtOAc to provide the desired product.

1-phenylazetidin-2-one:[23] To a suspension of aniline (10 mmol) and K_2CO_3 (13 mmol) in 10 mL of DCM at 0 °C was added dropwise of 3-bromopropanoyl chloride (13 mmol). The mixture was stirred at 0 °C for minutes and allowed to warm up to room temperature for another 3 h. The reaction was quenched with water and extracted with EtOAc for three times. The combined organic layers were evaporated, and the residue was recrystallized in a hot solution of 1:1 petroleum ether/EtOAc to afford 3-bromo-N-phenylpropanamide as white crystals. This solid was then dissolved in DMF and cooled to 0 °C. To this solution was added 1.5 equiv of sodium *tert*-butoxide in one portion, and the mixture was allowed to warm up to room temperature gradually. The reaction was quenched with water after 3 h and extracted with EtOAc. The combined organic layers were evaporated, and the residue was purified by silica gel chromatography using a mixture of hexane and EtOAc to provide the desired product. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.34 (dd, *J* = 12.0, 5.1 Hz, 4H), 7.12-7.06 (m, 1H), 3.63 (t, *J* = 4.5 Hz, 2H), 3.12 (t, *J* = 4.5 Hz, 2H); MS (ESI/TOF) m/z: Calcd. for C_9H_9NO $[M]^+$ 147.07; Found: 147.07.

N-(toluene-4-sulfonyl) lactam:[24] To a solution of lactam (5mmol, 1.0 eq.) in THF (10mL) was added n-butyllithium (2.4 M, 2.3 mL, 1.1 eq.) at -78 °C under an atmosphere of nitrogen. The resulting mixture was stirred at -78 °C for 0.5 hr. A solution of p-toluenesulfonyl chloride (5.5 mmol, 1.1 eq.) in THF (5 mL) was added. The mixture was warmed to rt and stirred for 1.5 hr. Water was added and the layers were separated. The organic layer was washed successively with water then dried over magnesium sulfate, filtered, and the solvent was removed by evaporation in vacuum. The resulting residue was purified by silica gel chromatography using a mixture of hexane and EtOAc to provide the desired product.

1-(*tert*-butoxycarbonyl)-2-pyrrolidinone:[25] A solution of lactam (2.13 g, 25.03 mmol) in dry MeCN (12 ml) was cooled to 0°C; then a solution of di-*tert*-butyl dicarbonate (5.73 g, 26.25 mmol) in MeCN (8 ml) was added via syringe. DMAP (305 mg, 2.50 mmol) was added and the cooling bath was removed. After 2.5 h the reaction was concentrated in vacuum and the resulting residue was purified by silica gel chromatography using a mixture of hexane and EtOAc to provide the desired product as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.78-3.69 (m, 2H), 2.50 (t, *J* = 8.1 Hz, 2H), 2.05-1.92 (m, 2H), 1.52 (s, 9H).

1-(*tert*-butoxycarbonyl)-2-oxopiperidine:[26] Triethylamine (10 mmol), DMAP (1 mmol) and di-*tert*-butyl dicarbonate (15 mmol) were added to a stirring solution of lactam (10 mmol) in dichloromethane (20 mL). The solution was allowed to stir at room temperature for 3h. The reaction was then concentrated under reduced pressure to give an orange semi-solid. The semi-solid was then taken up in DCM and purified by flash chromatography on silica gel to a white crystalline solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.65 (t, *J* = 5.6 Hz, 2H), 2.51 (dd, *J* = 9.7, 3.9 Hz, 2H), 1.89-1.74 (m, 4H), 1.52 (s, 9H).

3-phenyloxazolidin-2-one:[27] To a mixture of aniline (5mmol, 1.0 eq.) and ethylene carbonate (5 g) in 50 mL of schlenk flask was added DABCO (10mmol, 2.0 eq.) under an atmosphere of nitrogen. The resulting mixture was stirred at 100 oC for 16 hrs. Water was added and the mixture was extracted with DCM for 3 times and the organic layer was combined, washed successively with water and brine then dried over magnesium sulfate, filtered, and the solvent was removed by evaporation in vacuo. The resulting residue was purified by silica gel chromatography using a mixture of hexane and EtOAc to provide the desired product. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.54 (dd, *J* = 8.7, 1.0 Hz, 2H), 7.43-7.34 (m, 2H), 7.14 (t, *J* = 7.4 Hz, 1H), 4.48 (dd, *J* = 8.8, 7.1 Hz, 2H), 4.06 (dd, *J* = 8.8, 7.2 Hz, 2H); MS (ESI/TOF) m/z: Calcd. for $C_9H_9NO_2$ $[M]^+$ 163.06; Found: 163.06.

General procedure for the hydrogenation of lactams: In a glove box, Ru-pincer complex (1 mol%), K_3PO_4 (10 mol%) and lactam (0.5 mmol) was added to a 125-mL autoclave, anhydrous THF (2 mL) was then injected via a syringe. The reaction vessel was sealed and purged three times with hydrogen gas. Then the pressure of H_2 in the autoclave was increased to 50 atm. The mixture was heated at 150 °C for 24 h, and cooled to room temperature. After H_2 was released in the fume hood, the solvent was removed under reduced pressure. The mixture was analyzed by NMR analysis and the yield was determined by the incompletely consumed reagents.

4-(phenylamino)butan-1-ol (7):[9a] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.17 (d, *J* = 7.5 Hz, 2H), 6.70 (t, *J* = 7.3 Hz, 1H), 6.62 (d, *J* = 8.1 Hz, 2H), 3.70 (t, *J* = 5.6 Hz, 2H), 3.16 (t, *J* = 6.2 Hz, 2H), 1.71 (dd, *J* = 8.6, 5.7 Hz, 4H); MS (ESI/TOF) m/z: Calcd. for $C_{10}H_{15}NO$ $[M]^+$ 165.11; Found: 165.11.

3-(phenylamino)propan-1-ol (8):[9a] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.22 – 7.15 (m, 1H), 6.76-6.68 (m, 0H), 6.65 (dd, *J* = 8.6, 1.0 Hz, 1H), 3.82 (t, *J* = 5.9 Hz, 1H), 3.29 (t, *J* = 6.5 Hz, 1H), 1.93-1.85 (m, 1H); MS (ESI/TOF) m/z: Calcd. for $C_9H_{13}NO$ $[M]^+$ 151.10; Found: 151.10.

5-(phenylamino)pentan-1-ol (9):[9a] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.22-7.14 (m, 2H), 6.73-6.66 (m, 1H), 6.65-6.57 (m, 2H), 3.68 (t, *J* = 6.4 Hz, 2H), 3.14 (t, *J* = 7.0 Hz, 2H), 1.65 (tt, *J* = 13.6, 7.0 Hz, 5H), 1.55-1.45 (m, 2H); MS (ESI/TOF) m/z: Calcd. for $C_{11}H_{17}NO$ $[M]^+$ 179.13; Found: 179.13.

6-(phenylamino)hexan-1-ol (10):[9a] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.21-7.13 (m, 2H), 6.73-6.65 (m, 1H), 6.60 (dd, *J* = 8.6, 0.9 Hz, 2H), 3.65 (dd, *J* = 11.9, 6.5 Hz, 2H), 3.11 (dd, *J* = 12.9, 7.0 Hz, 2H), 1.69-1.58 (m, 4H), 1.48-1.38 (m, 4H); MS (ESI/TOF) m/z: Calcd. for $C_{12}H_{19}NO$ $[M]^+$ 193.15; Found: 193.15.

5-(*o*-tolylamino)pentan-1-ol (11a):[9a] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.44 (d, *J* = 7.7 Hz, 1H), 7.37 (t, *J* = 7.8 Hz, 1H), 6.78-6.66 (m, 2H), 4.31 (s, 1H), 3.69 (dd, *J* = 11.1, 6.2 Hz, 2H), 3.20 (dd, *J* = 12.4, 6.9 Hz, 2H), 1.72 (dt, *J* = 14.4, 7.1 Hz, 2H),

1.68-1.57 (m, 3H), 1.56-1.46 (m, 2H), 1.31 (s, 1H); MS (ESI/TOF) m/z: Calcd. for $C_{12}H_{19}NO$ $[M]^+$ 193.15; Found: 193.15.

5-(*m*-tolylamino)pentan-1-ol (11b):[9a] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.07 (td, *J* = 7.4, 1.2 Hz, 2H), 6.53 (d, *J* = 7.2 Hz, 1H), 6.43 (d, *J* = 7.1 Hz, 2H), 3.67 (t, *J* = 6.3 Hz, 2H), 3.13 (t, *J* = 7.0 Hz, 2H), 2.28 (s, 3H), 1.67-1.61 (m, 4H), 1.54-1.46 (m, 2H); MS (ESI/TOF) m/z: Calcd. for $C_{12}H_{19}NO$ $[M]^+$ 193.15; Found: 193.15.

5-(*p*-tolylamino)pentan-1-ol (11c):[9a] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.98 (d, *J* = 8.3 Hz, 2H), 6.53 (d, *J* = 8.4 Hz, 2H), 3.66 (dd, *J* = 11.3, 6.2 Hz, 2H), 3.11 (t, *J* = 6.9 Hz, 2H), 2.23 (s, 3H), 1.64 (ddd, *J* = 11.7, 11.0, 5.7 Hz, 4H), 1.53-1.42 (m, 2H); MS (ESI/TOF) m/z: Calcd. for $C_{12}H_{19}NO$ $[M]^+$ 193.15; Found: 193.15.

4-(*m*-tolylamino)butan-1-ol (12):[9a] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.07 (t, *J* = 7.4 Hz, 1H), 6.54 (d, *J* = 7.1 Hz, 1H), 6.45 (s, 2H), 3.70 (s, 2H), 3.15 (s, 2H), 2.28 (s, 3H), 1.70 (s, 4H); MS (ESI/TOF) m/z: Calcd. for $C_{11}H_{17}NO$ $[M]^+$ 179.13; Found: 179.13.

5-((2-methoxyphenyl)amino)pentan-1-ol (13a):[9a] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.87 (td, *J* = 7.6, 1.1 Hz, 1H), 6.76 (dd, *J* = 7.9, 1.2 Hz, 1H), 6.64 (ddd, *J* = 16.7, 11.5, 4.6 Hz, 2H), 4.17 (s, 1H), 3.84 (s, 3H), 3.67 (d, *J* = 3.2 Hz, 2H), 3.14 (dd, *J* = 13.0, 6.9 Hz, 2H), 1.66 (dd, *J* = 18.7, 7.5 Hz, 4H), 1.54-1.47 (m, 2H); MS (ESI/TOF) m/z: Calcd. for $C_{12}H_{19}NO_2$ $[M]^+$ 209.14; Found: 209.14.

5-((3-methoxyphenyl)amino)pentan-1-ol (13b):[9a] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.07 (t, *J* = 8.1 Hz, 1H), 6.24 (ddd, *J* = 15.8, 8.1, 2.1 Hz, 2H), 6.15 (t, *J* = 2.3 Hz, 1H), 3.77 (s, 3H), 3.67 (t, *J* = 6.4 Hz, 2H), 3.12 (t, *J* = 7.0 Hz, 2H), 1.64 (ddd, *J* = 12.9, 11.4, 7.0 Hz, 4H), 1.48 (tdd, *J* = 9.3, 6.3, 3.3 Hz, 2H); MS (ESI/TOF) m/z: Calcd. for $C_{12}H_{19}NO_2$ $[M]^+$ 209.14; Found: 209.14.

5-((2-(trifluoromethyl)phenyl)amino)pentan-1-ol (14a):[9a] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.12 (t, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 7.2 Hz, 1H), 6.68-6.55 (m, 2H), 3.68 (dd, *J* = 11.8, 6.3 Hz, 2H), 3.17 (dd, *J* = 12.7, 6.9 Hz, 2H), 1.68 (ddd, *J* = 20.2, 14.7, 7.2 Hz, 4H), 1.55-1.47 (m, 2H) ; ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.44; MS (ESI/TOF) m/z: Calcd. for $C_{12}H_{16}F_3NO$ $[M]^+$ 247.12; Found: 247.12.

5-((4-(trifluoromethyl)phenyl)amino)pentan-1-ol (14b):[9a] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.39 (d, *J* = 8.5 Hz, 2H), 6.58 (d, *J* = 8.5 Hz, 2H), 3.98 (s, 1H), 3.68 (dd, *J* = 11.6, 6.3 Hz, 2H), 3.16 (dd, *J* = 12.8, 6.8 Hz, 2H), 1.73-1.60 (m, 4H), 1.50 (ddd, *J* = 14.3, 8.5, 4.9 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.94; MS (ESI/TOF) m/z: Calcd. for $C_{12}H_{16}F_3NO$ $[M]^+$ 247.12; Found: 247.12.

4-((4-(trifluoromethyl)phenyl)amino)butan-1-ol (15):[9a] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.39 (d, *J* = 8.5 Hz, 2H), 6.59 (d, *J* = 8.5 Hz, 2H), 4.06 (s, 1H), 3.73-3.68 (m, 1H), 3.19 (t, *J* = 6.3 Hz, 2H), 1.78-1.64 (m, 4H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.96; MS (ESI/TOF) m/z: Calcd. for $C_{11}H_{14}F_3NO$ $[M]^+$ 233.10; Found: 233.10.

4-((2-fluorophenyl)amino)butan-1-ol (16):[9a] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.97 (ddd, *J* = 14.9, 11.8, 8.1 Hz, 2H), 6.70 (t, *J* = 8.4 Hz, 1H), 6.62 (ddd, *J* = 12.9, 6.4, 2.5 Hz, 1H), 3.72 (d, *J* = 8.4 Hz, 2H), 3.19 (q, *J* = 6.3 Hz, 2H), 1.79-1.67 (m, 4H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -136.83; MS (ESI/TOF) m/z: Calcd. for $C_{10}H_{14}FNO$ $[M]^+$ 183.11; Found: 183.11.

5-((2-fluorophenyl)amino)pentan-1-ol (17):[9a] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.04-6.91 (m, 2H), 6.68 (t, *J* = 8.4 Hz, 1H), 6.64-6.55 (m, 1H), 3.86 (s, 1H), 3.68 (dd, *J* = 11.7, 6.3 Hz, 2H), 3.16 (dd, *J* = 13.0, 6.8 Hz, 2H), 1.67 (ddd, *J* = 22.8, 15.2, 7.8 Hz, 4H), 1.51 (ddd, *J* = 8.9, 4.7, 1.4 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -136.99; MS (ESI/TOF) m/z: Calcd. for $C_{11}H_{16}FNO$ $[M]^+$ 197.12; Found: 197.12.

5-((2-chlorophenyl)amino)pentan-1-ol (18):[9c] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.11 (d, *J* = 8.8 Hz, 2H), 6.51 (d, *J* = 8.8 Hz, 2H), 3.67 (t, *J* = 6.4 Hz, 3H), 3.09 (t, *J* = 7.0 Hz, 2H), 1.68-1.59 (m, 4H), 1.51-1.45 (m, 2H); MS (ESI/TOF) m/z: Calcd. for $C_{11}H_{16}ClNO$ $[M]^+$ 213.09; Found: 213.09.

5-(naphthalen-1-ylamino)pentan-1-ol (19):[9c] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.79 (dd, *J* = 7.8, 6.3 Hz, 2H), 7.48-7.38 (m, 2H), 7.35 (t, *J* = 7.9 Hz, 1H), 7.22 (d, *J* = 8.2 Hz, 1H), 6.61 (d, *J* = 7.5 Hz, 1H), 4.32 (s, 1H), 3.70 (t, *J* = 6.3 Hz, 2H), 3.30 (t, *J* = 7.1 Hz, 2H), 1.82 (dd, *J* = 14.7, 7.3 Hz, 2H), 1.65 (ddd, *J* = 24.8, 14.5, 7.0 Hz, 4H); MS (ESI/TOF) m/z: Calcd. for $C_{15}H_{19}NO$ $[M]^+$ 229.15; Found: 229.15.

4-(pyridin-3-ylamino)butan-1-ol (20):[9c] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.01 (d, *J* = 2.5 Hz, 1H), 7.93 (dd, *J* = 4.6, 1.2 Hz, 1H), 7.07 (dd, *J* = 8.2, 4.6 Hz, 1H), 6.91-6.82 (m, 1H), 3.71 (d, *J* = 6.1 Hz, 2H), 3.17 (t, *J* = 6.5 Hz, 2H), 1.70 (dd, *J* = 8.5, 3.7 Hz, 4H); MS (ESI/TOF) m/z: Calcd. for $C_9H_{14}N_2O$ $[M]^+$ 166.11; Found: 166.11.

5-(pyridin-3-ylamino)pentan-1-ol (21):[9c] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.00 (d, *J* = 2.7 Hz, 1H), 7.93 (d, *J* = 4.6 Hz, 1H), 7.07 (dd, *J* = 8.2, 4.6 Hz, 1H), 6.85 (dd, *J* = 8.3, 1.6 Hz, 1H), 3.67 (s, 2H), 3.14 (dd, *J* = 12.9, 6.8 Hz, 2H), 1.70 (d, *J* = 7.6 Hz, 2H), 1.64-1.58 (m, 2H), 1.53-1.47 (m, 2H); MS (ESI/TOF) m/z: Calcd. for $C_{10}H_{16}N_2O$ $[M]^+$ 180.13; Found: 180.13.

2-(phenylamino)ethanol (23):[9c] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.20 (dd, *J* = 8.5, 7.4 Hz, 2H), 6.75 (td, *J* = 7.3, 1.0 Hz, 1H), 6.66 (d, *J* = 8.4 Hz, 2H), 4.01 (s, 1H), 3.81 (t, *J* = 5.2 Hz, 2H), 3.29 (dd, *J* = 10.7, 5.5 Hz, 2H), 2.32 (s, 1H); MS (ESI/TOF) m/z: Calcd. for $C_8H_{11}NO$ $[M]^+$ 137.08; Found: 137.08.

N-(4-hydroxybutyl)-4-methylbenzenesulfonamide (24):[9c] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.74 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 4.86 (t, *J* = 5.8 Hz, 0H), 3.62 (t, *J* = 5.7 Hz, 2H), 2.97 (q, *J* = 6.3 Hz, 2H), 2.42 (s, 3H), 1.59-1.52 (m, 4H); MS (ESI/TOF) m/z: Calcd. for $C_{11}H_{17}NO_3S$ $[M]^+$ 243.09; Found: 243.09.

N-(5-hydroxypentyl)-4-methylbenzenesulfonamide (25):[9c] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.74 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 3.59 (t, *J* = 6.4 Hz, 2H), 2.93 (t, *J* = 6.9 Hz, 2H), 2.42 (s, 2H), 1.56-1.42 (m, 4H), 1.41-1.28 (m, 2H); MS (ESI/TOF) m/z: Calcd. for $C_{12}H_{19}NO_3S$ $[M]^+$ 257.11; Found: 257.11.

N-(6-hydroxyhexyl)-4-methylbenzenesulfonamide (26):[9c] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.74 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* =

8.0 Hz, 2H), 3.60 (t, *J* = 6.5 Hz, 2H), 2.93 (t, *J* = 7.0 Hz, 2H), 2.43 (s, 3H), 1.49 (ddd, *J* = 13.9, 9.9, 6.9 Hz, 4H), 1.35-1.27 (m, 4H); MS (ESI/TOF) m/z: Calcd. for $C_{13}H_{21}NO_3S$ $[M]^+$ 271.12; Found: 271.12.

***tert*-Butyl (4-hydroxybutyl)carbamate (27)**:[9c] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.93 (s, 1H), 3.56 (s, 2H), 3.30 (s, 1H), 3.06 (s, 2H), 1.50 (s, 4H), 1.37 (s, 9H); MS (ESI/TOF) m/z: Calcd. for $C_9H_{19}NO_3$ $[M]^+$ 189.14; Found: 189.14.

***tert*-Butyl (5-hydroxypentyl)carbamate (28)**:[9c] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.64 (s, 2H), 3.32 (d, *J* = 4.6 Hz, 1H), 3.12 (d, *J* = 6.2 Hz, 2H), 2.37 (t, *J* = 6.3 Hz, 1H), 1.88-1.73 (m, 2H), 1.66-1.56 (m, 2H), 1.52-1.48 (m, 2H), 1.43 (s, 9H); MS (ESI/TOF) m/z: Calcd. for $C_{10}H_{21}NO_3$ $[M]^+$ 203.15; Found: 203.15.

6-aminohexan-1-ol (29):[9c] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.63 (t, *J* = 6.6 Hz, 2H), 2.68 (t, *J* = 6.9 Hz, 2H), 1.56 (dd, *J* = 13.6, 7.0 Hz, 2H), 1.48-1.42 (m, 2H), 1.39-1.33 (m, 4H); MS (ESI/TOF) m/z: Calcd. for $C_6H_{15}NO$ $[M]^+$ 117.11; Found: 117.11.

7-aminoheptan-1-ol (30):[9c] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.64 (t, *J* = 6.6 Hz, 2H), 2.68 (t, *J* = 7.0 Hz, 2H), 1.57 (dt, *J* = 13.6, 6.8 Hz, 4H), 1.50-1.34 (m, 6H); MS (ESI/TOF) m/z: Calcd. for $C_7H_{17}NO$ $[M]^+$ 131.13; Found: 131.13.

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Conflict of interest

The authors declare no conflict of interest.

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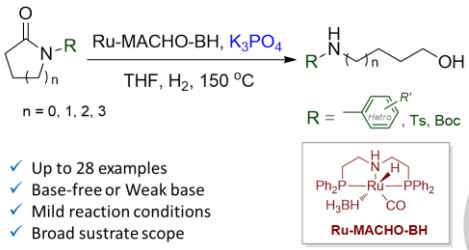
By using ruthenium pincer complex (Ru-MACHO-BH) as a catalyst, the challenging hydrogenation of lactams has been realized to successfully delivery corresponding value-added aminoalcohols in good to excellent yields under relatively mild reaction conditions.



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