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Synthesis of Symmetric and Unsymmetric Secondary Amines from the Ligand Promoted Ruthenium Catalyzed Deaminative Coupling Reaction of Primary Amines

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Abstract

The catalytic system generated *in-situ* from the tetranuclear Ru–H complex with a catechol ligand (**1/L1**) was found to be effective for the direct deaminative coupling of two primary amines to form secondary amines. The catalyst **1/L1** was highly chemoselective for promoting the coupling of two different primary amines to afford unsymmetric secondary amines. The analogous coupling of aniline with primary amines formed aryl-substituted secondary amines. The treatment of aniline-*d*₇ with 4-methoxybenzylamine led to the coupling product with significant deuterium incorporation on CH₂ (18% D). The most pronounced carbon isotope effect was observed on the α-carbon of the product isolated from the coupling reaction of 4-methoxybenzylamine (C(1) = 1.015(2)). Hammett plot was constructed from measuring the rates of the coupling reaction of 4-methoxyaniline with a series of *para*-substituted benzylamines 4-X-C₆H₄CH₂NH₂ (X = OMe, Me, H, F, CF₃). (ρ = −0.79 ± 0.1). A plausible mechanistic scheme has been proposed for the coupling reaction on the basis of these results. The catalytic coupling method provides an operationally simple and chemoselective synthesis of secondary amine products without using any reactive reagents or forming wasteful byproducts.

Graphical Abstract

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Notes

The authors declare no competing financial interest.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental procedures, spectroscopic data and NMR spectra (PDF)

Keywords

secondary amine; deamination; ruthenium catalyst

Introduction

Designing catalytic C–N bond cleavage methods has attracted considerable research efforts in the field of homogeneous catalysis since such methods are of fundamental importance in a variety of industrial chemical syntheses as well as in biochemical processes of nitrogen compounds.¹ Even though catalytic C–N bond cleavage methods have been recognized as an essential protocol for harnessing nitrogen compounds from both petroleum and biomass feedstocks, these catalytic methods have long been hampered by a relatively strong C–N bond strength and catalyst poisoning by the nitrogen substrates.² In a pioneering report, Fujiwara and co-workers first demonstrated the direct coupling of olefins with arylamines, in which arene sp^2 C–N bond cleavage was promoted by a stoichiometric amount of Pd(II) salts.³ More recently, Kakiuchi and co-workers devised a ruthenium-catalyzed C–C coupling reaction of arylamines with organoboranes, by exploiting a directing group assisted sp^2 C–N bond activation strategy.⁴ A few remarkably efficient amide-to-ester conversion methods via amide C–N bond cleavage have been achieved by using Ni catalysts.⁵ A number of Pd-catalyzed C–N cleavage methods have also been developed, including intramolecular Heck-type coupling reactions⁶ and allylamine coupling reactions.⁷ Selective catalytic C–C coupling methods via sp^3 C–N bond activation of allyl- and benzylic amines have been achieved.⁸ Other notable examples of catalytic C–N bond cleavage reactions include: oxidative C–H coupling reaction of amides with alkynes,⁹ and Milstein group's report on the Ru-catalyzed hydrogenolysis of amides.¹⁰ Catalytic C–N cleavage methods have also been successfully utilized for constructing nitrogen heterocycles.¹¹

Chemoselective synthesis of amines has long been a pertinent issue in organic synthesis. Much research efforts has been devoted to the development of new catalytic synthesis of amines, and transition metal catalyzed dehydrogenative coupling strategies have emerged as highly effective ways to activate amines and alcohols.¹² In particular, late transition metal catalysts have been successfully employed to promote amine-to-alcohol coupling reactions via hydrogen borrowing strategy to synthesize unsymmetric secondary amines.¹³ Traditionally, the reductive amination methods have also been commonly used for the synthesis of secondary amines.¹⁴ Since these methods often require stoichiometric reducing agents and/or additives, which result in the formation of copious amounts of salt byproducts, catalytic deaminative coupling methods have been recognized as an alternative strategy for the synthesis of secondary amines. Beller and co-workers reported a highly selective dealkylation of amines by using Shvo catalyst.¹⁵ Zhang group also devised the synthesis of unsymmetric secondary amines from the coupling of aniline with primary amines by using soluble Co catalysts.¹⁶ From both economic and environmental perspectives, the development of chemoselective catalytic coupling methods via C–N bond cleavage of amines and related nitrogen compounds still remains an essential goal in the fields of homogeneous catalysis and organic synthesis.

We previously disclosed the synthesis of unsymmetrical ethers from the dehydrative coupling reactions of alcohols and aldehydes that are catalyzed by a well-defined cationic ruthenium-hydride complex.¹⁷ Since these coupling reactions are driven by the formation of water, we reasoned that the analogous deaminative coupling reactions of amines could be achieved, where the formation of ammonia would serve as the driving force for such coupling reactions. Herein, we report the synthesis of symmetric and unsymmetric secondary amines from the catalytic deaminative coupling of primary amines. The catalytic method exhibits high chemoselectivity as well as a broad substrate scope in forming secondary amines, while generating ammonia as the only byproduct.

Results and Discussion

We previously devised a catalytic system comprised of the cationic Ru–H complex and a phenol ligand, which was found to exhibit high catalytic activity for the hydrogenolysis of carbonyl compounds to yield the corresponding aliphatic products.¹⁸ By adopting the similar ligand controlled catalysis strategy, we initially screened soluble Ru catalysts with phenol and related oxygen and nitrogen ligands to promote the C–N bond activation reactions. We have chosen the coupling reaction of benzylamine with cyclohexylamine as a test case to screen both Ru catalysts and the ligands (eq 1).

(1)

Among the initially screened Ru catalysts, both the tetranuclear Ru–H complex $[(\text{PCy}_3)(\text{CO})\text{RuH}]_4(\text{O})(\text{OH})_2$ (**1**) and the cationic $[(\text{C}_6\text{H}_6)(\text{PCy}_3)(\text{CO})\text{RuH}]^+\text{BF}_4^-$ (**2**) with 1,2-catechol ligand exhibited the most promising activity for the coupling reaction, as analyzed by both GC and NMR spectroscopic methods (Table 1). Among the screened oxygen and nitrogen ligands, 4-(1,1-dimethylethyl)-1,2-benzenediol (**L1**) was found to give the highest activity and selectivity for these Ru catalysts in giving the unsymmetric amine product **3a** over the symmetric one **4a** (entries 9 and 13). After further ligand screening and optimization studies, we have chosen the standard condition for the 1.0 mmol scale coupling reaction as: **1** (0.75 mol %, 3 Ru mol %)/**L1** (10 mol %) in chlorobenzene (2 mL) at 130 °C (Tables S1 and S2, Supporting Information (SI)). A 3:1 ratio of catechol ligand to Ru catalyst was found to be the optimum for the catalytic activity, as a lower ratio (2:1) typically gave a lower product yield. Non-protic polar solvents such as chlorobenzene and dioxane afforded the highest product yields and selectivity, and for the sake of consistency, we have chosen chlorobenzene as the solvent for all coupling reactions. The

formation of the byproduct ammonia was detected in the crude mixture as analyzed by both NMR and GC-MS methods.

We explored the substrate scope of the deaminative coupling reaction by using the optimized catalyst system **1/L1** under the standard condition (Table 2). The coupling of benzylic amines with a variety of aliphatic and benzylic primary amines selectively formed the unsymmetric secondary amine products **3a–3m**. An excess amount (1.4 equiv) of the second amine (usually more electron rich amine) was found to improve the product selectivity for unsymmetric amines **3**. Typically, <20 % of the symmetric amine products was formed in the crude mixture in most cases, and analytically pure unsymmetric amine products were readily isolated after silica gel column chromatographic separation. The major byproducts, symmetric amine products **4** were detected by TLC and GC/MS, but were not isolated in these cases. The coupling of phenethyl amines with both benzylic and aliphatic amines also gave the selective formation of **3n–3v**. Indole-, Furanyl- and phenol-substituted amines with cyclohexylamine selectively yielded the unsymmetric secondary amine products **3bb–3dd**. For these cases, the coupling of benzylic and other aryl-substituted amines with electron-rich amines tend to favor the formation of unsymmetrical amines over the symmetrical ones. In contrast, the coupling of two different aliphatic amines with sterically non-demanding group yielded in a mixture of symmetric and unsymmetric amines. The coupling reaction with secondary and tertiary amines was found to be very sluggish and unselective, resulting in a complex mixture of products. The catalytic coupling method is operationally simple and exhibits high chemoselectivity toward the formation of unsymmetric secondary amines without resorting to employing any reactive reagents.

We next explored the substrate scope for the formation of symmetric secondary amines by using the catalyst system **1/L1** (Table 3). Benzylic primary amines reacted smoothly to afford the secondary amine products **4a–4k** without the formation of tertiary amines or other side products. The coupling of both phenethyl and indanyl amines formed the corresponding secondary amine products **4m–4r**. While cyclohexyl and thiophene-substituted amines predictively yielded the corresponding secondary amine products **4s** and **4t**, respectively, a mixture of secondary and tertiary amines was formed for sterically non-demanding aliphatic amines **4u–4x**. Generally, the coupling of chiral primary amines led to a 1:1 diastereomeric mixture of products as illustrated by the formation of **4p–4q**, but interestingly, a diastereoselective formation of the product **4l** was obtained in case of (*R*)-4-methoxy- α -methylbenzenemethanamine (d.r. = 7:1). The catalytic method delivers a operationally simple synthesis of symmetric secondary amines from readily available primary amines without using any reactive reagents via a deaminative coupling method.^{14,16}

To further illustrate the synthetic versatility of catalytic coupling method, we next explored the coupling reaction of aniline derivatives with primary amine substrates of biological relevance (Table 4). The coupling of *para*-substituted anilines with benzylic amines led to the selective formation of unsymmetric amine products **5a–5e** without any significant amount of the symmetric amine products. Similarly, the reaction of *para*-substituted anilines with 3,4,5-trimethoxybenzylamine afforded the coupling products **5f–5h** in high yields. Single crystals of **5f** were obtained by slow evaporation in CH₂Cl₂/hexanes, and its structure was determined by X-ray crystallography.

The treatment of 3-amino-9-ethylcarbazole with *n*-hexylamine predictively yielded the product **5q**. The coupling of (*R*)-(+)-aminogluthathimide with 3,4,5-trimethoxybenzylamine led to the optically active coupling product (*R*)-**5r**, without any detectable racemization. The coupling of L-glutamine with 3-phenylpropylamine and 4-methoxybenzylamine led to the cyclized amine products **5s** and **5t** in 75% and 70% yields, respectively. The formation of cyclized products **5s** and **5t** can be rationalized by initial dehydrative cyclization of glutamine followed by the deaminative coupling with the primary amine substrates. The optimized standard conditions were used for all of these coupling reactions as described in Tables 2–4, with slight modifications on the reaction time and temperature.

We monitored the amine coupling reaction by NMR spectroscopy to probe the overall reaction profile. In a J-Young NMR tube equipped with Teflon stopcock, 4-methoxybenzylamine (34 mg, 0.25 mmol) and the catalyst system **1** (3 mg, 0.75 mol %)/**L1** (4 mg, 10 mol %) were dissolved in toluene-*d*₈ (0.5 mL). The tube was immersed in an oil bath at 130 °C, and the reaction progress was monitored by ¹H NMR in 20 min intervals.

As shown in Figure 1, the secondary amine product **4c** was formed steadily at the expense of the benzylamine substrate. Initially, the formation of a minor product was also observed (~10%), which gradually disappeared within 200 min of the reaction time. The structure of minor product was subsequently determined to be ArCH=NCH₂Ar (Ar = 4-methoxyphenyl) by both NMR and GC/MS, as obtained from a separate preparatory scale experiment.

(2)

Next, we examined the deuterium labeling pattern on the product from the reaction of aniline-*d*₇ with 4-methoxybenzylamine (eq 2). The reaction tube consisted of aniline-*d*₇ (50 mg, 0.5 mmol) with 4-methoxybenzylamine (69 mg, 0.5 mmol) in the presence of **1** (7 mg, 0.75 mol %)/**L1** (8 mg, 10 mol %) in chlorobenzene (1 mL) was heated in an oil bath at 140 °C for 20 h. The product **5a-d** was isolated by silica gel column chromatography, and its deuterium content was analyzed by ¹H and ²H NMR (Figure S1, SI). A significant amount of deuterium was incorporated to the CH₂ position of **5a-d** (18% D), without any deuterium exchange on the arene C–H positions. In a control experiment, the treatment of the isolated product **5a** with aniline-*d*₇ in the presence of **1** (0.75 mol %)/**L1** (10 mol %) did not lead to any significant deuterium exchange into the benzyl position of **5a** under similar reaction conditions after 20 h. The significant amount of the deuterium incorporation suggests that the imine-to-amine hydrogenation-dehydrogenation process might have occurred during the product formation of **5a**.

(3)

To discern the rate-limiting step of the catalytic reaction, we employed Singleton's high precision NMR technique to measure the carbon isotope effect for the coupling reaction (eq 3).¹⁹ The reaction tube of 4-methoxybenzylamine (2 mmol) and **1** (0.75 mol %)/**L1** (10 mol %) in chlorobenzene (4 mL) was heated at 130 °C for 16 h for high conversion and for 2–3 h for low conversion cases. The product **4c** was isolated by a column chromatography on silica gel, and was analyzed by ¹³C NMR. The most pronounced carbon isotope effect was observed on the α-carbon of the product **4c** when the ¹³C ratio of the product at three high conversions (86–89%) was compared with the sample obtained at low conversions (12–15%) [(average of ¹³C at 87% conversion)/(average of ¹³C at 13% conversion) at C(1) = 1.015(2)] (Table S2, SI).

The significant carbon isotope effect on the α-CH₂ carbon is consistent with the C–N bond cleavage turnover-limiting step. In support of this notion, Singleton and co-workers showed that the observation of most pronounced carbon isotope effect has been a definitive tool for establishing the rate-limiting step for both C–C and C–O bond forming reactions.^{19c} While C–N bond cleavage has been found to be the turnover limiting step for a number of chemical and biochemical coupling reactions,²⁰ very few carbon kinetic isotope effect measurements have been reported for the catalytic coupling reactions of nitrogen compounds. Eubanks and co-workers measured pronounced carbon isotope effects in Hofmann elimination reaction of *para*-substituted (2-phenylethyl)-trimethylammonium bromides, which indicated an E2 mechanism involving C–N bond cleavage step.²¹ In a urease-catalyzed hydrolysis of hydroxyurea, Cleland and co-workers observed the significant carbon isotope effect on the carbonyl carbon but not on the nitrogen atom, which argues for the formation of a common intermediate prior to the C–N bond cleavage step.²²

The Hammett plot was constructed from measuring the rate of the coupling reaction of a series of *para*-substituted benzylamines 4-X-C₆H₄CH₂NH₂ (X = OMe, Me, H, Cl, F, CF₃) in the presence of **1** (0.75 mol %)/**L1** (10 mol %) in toluene-*d*₈ (Figure 2). The rate of each substrate was obtained by measuring the appearance of the product peaks, which were normalized against an internal standard (C₆Me₆) as analyzed by ¹H NMR. The *k*_{obs} for each catalytic run was determined from a first order plot of *ln*[(benzylamine)_{*t*}]/(benzylamine)₀] vs time. The Hammett plot of log(*k*_X/*k*_H) vs σ_p showed a linearly correlated pattern with ρ = −0.79 ± 0.1. A relatively high negative slope suggests a significant cationic character build-up on the amine substrate during the coupling reaction.

We present a plausible mechanistic hypothesis for the deaminative coupling reaction on the basis of these results (Scheme 1). In light of the observation of imine product ArCH=NCH₂Ar, we propose the formation of a Ru-imine species **6** as a catalytically active species, which would be initially generated from the dehydrogenation of amine substrate.²³

In support of this notion, some oxidative C–N bond cleavage reactions are known to proceed via the formation of an imine intermediate.²⁴ The coordination of imine substrate to the Ru center would increase the electrophilic nature of the imine carbon, and the nucleophilic addition of the second amine substrate would proceed to form the Ru-1,1-diamine species **7**. Many structurally similar transition metal-urea complexes have been synthesized and their bonding and reactivity patterns have been well established.²⁵ The observation of carbon isotope effect provides an experimental support for the rate-limiting C–N cleavage step in forming the Ru-aminoalkyl species **8**. The dehydrogenation of second amine substrate in conjunction with the hydrogen transfer would form the coupling product **4** with the regeneration of imine species **6**. Both the detection of imine product and the selective deuterium incorporation on the α -CH₂ of **5a** suggest that the dehydrogenation and hydrogen transfer steps are likely facile and reversible under the reaction conditions.

Conclusion

In conclusion, we successfully devised a highly chemoselective synthesis of secondary amines from the deaminative coupling of primary amines. The catechol ligand promoted ruthenium catalytic system was found to exhibit a uniquely high activity and selectivity in forming both symmetric and unsymmetric secondary amines. The catalytic method has a number of salient features that it is operationally simple, exhibits a broad substrate scope, tolerates common organic functional groups, and forms ammonia as the sole byproduct without employing any reactive reagents. The kinetic and spectroscopic studies thus far indicate that the coupling reaction proceeds via the formation of imine species with the turnover limiting C–N bond cleavage step. At this time, we have not been able to ascertain the exact role of catechol ligand on promoting the Ru catalyst, and we are currently pursuing the detection and/or the isolation of catalytically relevant Ru-catechol species.²⁶ We are also devoting our efforts to extend synthetic utility of the catalytic method for the synthesis of nitrogen heterocycles of biological importance.

Experimental Section

General Information

All operations were carried out in a nitrogen-filled glove box or by using standard high vacuum and Schlenk techniques unless otherwise noted. All solvents used were freshly distilled over appropriate drying reagents. Chlorobenzene was distilled from purple solutions of sodium and benzophenone, and hexanes was dried over calcium hydride prior to use. All organic substrates were received from commercial sources and were used without further purification. The ¹H, ²H, ¹³C, and ³¹P NMR spectra were recorded on a Varian 400 MHz FT-NMR spectrometer, and the data are reported as: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, app = apparent; coupling constant(s) in Hz; integration. Mass spectra were recorded from Agilent 6850 GC-MS spectrometer by using a HP-5 (5% phenylmethylpolysiloxane) column (30 m, 0.32 mm, 0.25 μ m). High resolution mass spectra were obtained at the Mass Spectrometry/ICP Lab, Department of Chemistry and Biochemistry, University of Wisconsin-Milwaukee, Milwaukee, WI. Elemental analyses were performed at the Midwest Microlab, Indianapolis, IN.

General Procedure for the Catalytic Synthesis of Secondary Amines

In a glove box, complex **1** (13 mg, 0.75 mol %) and 4-(1,1-dimethylethyl)-1,2-benzenediol (**L1**), (16 mg, 10 mol %) were dissolved in chlorobenzene (1 mL) in a 25 mL Schlenk tube equipped with a Teflon screw cap stopcock and a magnetic stirring bar. The resulting mixture was stirred for 5 to 10 minutes until the solution turned to a reddish green color. In an alternative procedure, the complex **2** (17 mg, 3 mol %) and **L1** (16 mg, 10 mol %) were dissolved in anhydrous 1,4-dioxane (1 mL). Amine substrate (1.0 mmol and 1.4 mmol) in chlorobenzene (1 mL) was added to the reaction tube. After the tube was sealed, it was brought out of the glove box, and was stirred in an oil bath maintained at 130–140 °C for 16–20 h. The reaction tube was taken out of the oil bath, and was cooled to room temperature. After the tube was open to air, the solution was filtered through a short silica gel column by eluting with CH₂Cl₂ (10 mL), and the filtrate was analyzed by GC-MS. Analytically pure product was isolated by a simple column chromatography on silica gel (280–400 mesh, hexanes/EtOAc or hexanes/EtOAc/methanol).

Synthesis of Benzylcyclohexylamine (3a)

In a glove box, complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %) were dissolved in chlorobenzene (1 mL) in a 25 mL Schlenk tube equipped with a Teflon screw cap stopcock and a magnetic stirring bar. The resulting mixture was stirred for 5–10 min until the solution was turned reddish green color. Benzylamine (1.0 mmol) and cyclohexylamine (1.4 mmol) were dissolved in chlorobenzene (1 mL), and the solution was added to the reaction tube. The tube was brought out of the glove box, and was stirred in an oil bath maintained at 130 °C for 16 h. The reaction tube was taken out of the oil bath, and was cooled to room temperature. The resulting solution was filtered through a short silica gel column by eluting with CH₂Cl₂ (10 mL), and the filtrate was analyzed by GC-MS. Analytically pure product **3a** was isolated by a simple column chromatography on silica gel (280–400 mesh, *n*-hexane/EtOAc).

Synthesis of Dibenzylamine (4a)

In a glove box, complex **1** (13 mg, 0.75 mol %) and **L1** (16 mg, 10 mol %) were dissolved in chlorobenzene (1 mL) in a 25 mL Schlenk tube equipped with a Teflon screw cap stopcock and a magnetic stirring bar. The resulting mixture was stirred for 5 to 10 min until the solution was turned reddish green color. Benzylamine (107 mg, 1.0 mmol) in chlorobenzene (1 mL) was added to the reaction mixture. After the tube was sealed, it was brought out of the glove box, and was stirred in an oil bath maintained at 130 °C for 16 h. The reaction tube was taken out of the oil bath, and was cooled to room temperature. The resulting solution was filtered through a short silica gel column by eluting with CH₂Cl₂ (10 mL), and the filtrate was analyzed by GC-MS. Analytically pure product **4a** was isolated by a simple column chromatography on silica gel (280–400 mesh, *n*-hexane/EtOAc).

Catalyst and Ligand Screening Study

In a glove box, a Ru catalyst (3 mol % Ru atom) and a ligand (10 mol %) were dissolved in a solvent (1 mL) in a 25 mL Schlenk tube equipped with a Teflon screw cap stopcock and a magnetic stirring bar. After stirring for 5 to 10 min, benzylamine (54 mg, 0.5 mmol) and

cyclohexylamine (69 mg, 0.7 mmol) were dissolved in chlorobenzene (1 mL), and the solution was added to the reaction tube. The tube was brought out of the glove box, and was stirred in an oil bath at 130 °C for 16 h. The product yield was determined by ¹H NMR by using hexamethylbenzene as an internal standard. The results are summarized in Table S1 and S2.

***N*-Cyclohexylbenzenemethanamine (3a)**

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), benzylamine (107 mg, 1.0 mmol) and cyclohexylamine (139 mg, 1.4 mmol) was stirred at 130 °C for 16 h. The product **3a** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 138 mg, 73%). TLC; *R*_f = 0.3 (10% EtOAc in hexanes). Data for **3a**: ¹H NMR (400 MHz, CDCl₃) δ 7.35–7.29 (m, 4H), 7.28–7.20 (m, 1H), 3.81 (s, 2H), 2.49 (tt, *J* = 10.3, 3.7 Hz, 1H), 1.96–1.88 (m, 2H), 1.78–1.70 (m, 2H), 1.65–1.58 (m, 1H), 1.32–1.07 (m, 5H) ppm; ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 140.8, 128.3, 128.0, 126.7, 56.1, 51.0, 33.5, 26.1, 25.0 ppm; GC-MS for C₁₃H₁₉N, *m/z* = 189 (M⁺). ¹H and ¹³C NMR spectral data were in good agreement with the literature values.²⁷

***N*-Cyclohexyl-4-methoxybenzenemethanamine (3b)**

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), 4-methoxybenzylamine (137 mg, 1.0 mmol) and cyclohexylamine (139 mg, 1.4 mmol) was stirred at 130 °C for 16 h. The product **3b** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 171 mg, 78%). TLC; *R*_f = 0.3 (20% EtOAc in hexanes). Data for **3b**: ¹H NMR (400 MHz, CDCl₃) δ 7.25–7.21 (m, 2H), 6.88–6.83 (m, 2H), 3.79 (s, 3H), 3.74 (s, 2H), 2.47 (tt, *J* = 10.4, 3.7 Hz, 1H), 1.96–1.86 (m, 2H), 1.77–1.68 (m, 2H), 1.65–1.56 (m, 1H), 1.31 (br s, 1H), 1.30–1.05 (m, 5H) ppm; ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 158.4, 133.0, 129.2, 113.7, 56.0, 55.2, 50.4, 33.5, 26.1, 25.0 ppm; GC-MS for C₁₄H₂₁NO, *m/z* = 219 (M⁺). ¹H and ¹³C NMR spectral data were in good agreement with the literature values.²⁸

***N*-Cyclohexyl-4-fluorobenzenemethanamine (3c)**

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), 4-fluorobenzylamine (125 mg, 1.0 mmol) and cyclohexylamine (139 mg, 1.4 mmol) was stirred at 130 °C for 16 h. The product **3c** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 147 mg, 71%). TLC; *R*_f = 0.4 (20% EtOAc in hexanes). Data for **3c**: ¹H NMR (400 MHz, CDCl₃) δ 7.31–7.23 (m, 2H), 7.02–6.95 (m, 2H), 3.76 (s, 2H), 2.45 (tt, *J* = 10.3, 3.8 Hz, 1H), 1.94–1.85 (m, 2H), 1.77–1.68 (m, 2H), 1.64–1.56 (m, 1H), 1.37 (br s, 1H), 1.32–1.04 (m, 6H) ppm; ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 161.7 (d, *J*_{CF} = 244.2 Hz), 136.6 (d, *J*_{CF} = 3.1 Hz), 129.5 (d, *J*_{CF} = 7.9 Hz), 115.1 (d, *J*_{CF} = 21.2 Hz), 56.1, 50.2, 33.5, 26.1, 24.9 ppm; GC-MS for C₁₃H₁₈FN, *m/z* = 207 (M⁺). ¹H and ¹³C NMR spectral data were in good agreement with the literature values.²⁹

***N*-Cyclohexyl-4-(trifluoromethyl)benzenemethanamine (3d)**

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), 4-trifluoromethylbenzylamine (175 mg, 1.0 mmol) and cyclohexylamine (139 mg, 1.4

mmol) was stirred at 130 °C for 16 h. The product **3d** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 152 mg, 59%). TLC; R_f = 0.4 (20% EtOAc in hexanes). Data for **3d**: ^1H NMR (400 MHz, CDCl_3) δ 7.58–7.53 (m, 2H), 7.45–7.41 (m, 2H), 3.86 (s, 2H), 2.46 (tt, J = 10.3, 3.7 Hz, 1H), 1.95–1.86 (m, 2H), 1.77–1.69 (m, 2H), 1.64–1.56 (m, 1H), 1.30–1.05 (m, 5H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 145.1, 129.0 (q, J_{CF} = 32.2 Hz), 128.2, 125.2 (q, J_{CF} = 3.8 Hz), 124.3 (q, J_{CF} = 271.9 Hz), 56.2, 50.4, 33.5, 26.0, 24.9 ppm; GC-MS for $\text{C}_{14}\text{H}_{18}\text{F}_3\text{N}$, m/z = 257 (M^+). ^1H and ^{13}C NMR spectral data were in good agreement with the literature values.³⁰

***N*-(4-Chlorobenzyl)-2-(4-methoxyphenyl)ethanamine (3e)**

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), 4-chlorobenzylamine (141 mg, 1.0 mmol) and 4-methoxybenzeneethanamine (211 mg, 1.4 mmol) was stirred at 130 °C for 16 h. The product **3e** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 158 mg, 57%). TLC; R_f = 0.4 (20% EtOAc in hexanes). Data for **3e**: ^1H NMR (400 MHz, CDCl_3) δ 7.30–7.25 (m, 2H), 7.24–7.19 (m, 2H), 7.15–7.09 (m, 2H), 6.87–6.82 (m, 2H), 3.79 (s, 3H), 3.76 (s, 2H), 2.87–2.82 (m, 2H), 2.80–2.74 (m, 2H), 1.73 (br s, 1H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 157.9, 138.6, 132.5, 131.7, 129.5, 129.3, 128.4, 113.8, 55.1, 53.0, 50.5, 35.2 ppm; GC-MS for $\text{C}_{16}\text{H}_{18}\text{ClNO}$, m/z = 275 (M^+). HRMS (ESI-TOF) m/z : [$\text{M}+\text{H}$] $^+$ Calcd for $\text{C}_{16}\text{H}_{18}\text{ClNOH}$ 276.1150; Found 276.1122.

***N*-(Biphenyl-4-ylmethyl)hexan-1-amine (3f)**

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), 4-phenylbenzylamine (183 mg, 1.0 mmol) and 1-hexamine (141 mg, 1.4 mmol) was stirred at 130 °C for 16 h. The product **3f** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 176 mg, 66%). TLC; R_f = 0.3 (20% EtOAc in hexanes). Data for **3f**: ^1H NMR (400 MHz, CDCl_3) δ 7.61–7.54 (m, 4H), 7.46–7.37 (m, 4H), 7.36–7.31 (m, 1H), 3.83 (s, 2H), 2.66 (t, J = 7.3 Hz, 2H), 1.58–1.50 (m, 2H), 1.36–1.26 (m, 6H), 0.89 (t, J = 7.0 Hz, 3H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 141.0, 139.8, 139.6, 128.7, 128.5, 128.4, 127.1, 127.0, 53.7, 49.6, 31.8, 30.1, 27.0, 22.6, 14.1 ppm; GC-MS for $\text{C}_{19}\text{H}_{25}\text{N}$, m/z = 267 (M^+); HRMS (ESI-TOF) m/z : [$\text{M}+\text{H}$] $^+$ Calcd for $\text{C}_{19}\text{H}_{25}\text{NH}$ 268.2060; Found 268.2061.

Benzo[d][1,3]dioxol-5-yl-*N*-(biphenyl-4-ylmethyl)methanamine (3g)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), 4-phenylbenzylamine (183 mg, 1.0 mmol) and 1,3-benzodioxol-5-ylmethylamine (211 mg, 1.4 mmol) was stirred at 130 °C for 16 h. The product **3g** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 178 mg, 56%). TLC; R_f = 0.3 (20% EtOAc in hexanes). Data for **3g**: ^1H NMR (400 MHz, CDCl_3) δ 7.62–7.55 (m, 4H), 7.47–7.39 (m, 4H), 7.37–7.32 (m, 1H), 6.90–6.88 (m, 1H), 6.82–6.76 (m, 2H), 5.95 (s, 2H), 3.84 (s, 2H), 3.75 (s, 2H), 1.67 (br s, 1H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 147.7, 146.5, 140.9, 139.9, 139.3, 134.2, 128.7, 128.6, 127.1, 127.1, 127.0, 121.2, 108.7, 108.0, 100.9, 52.9, 52.6 ppm; GC-MS for $\text{C}_{21}\text{H}_{19}\text{NO}_2$, m/z = 317 (M^+); HRMS (ESI-TOF) m/z : [$\text{M}+\text{H}$] $^+$ Calcd for $\text{C}_{21}\text{H}_{19}\text{NO}_2\text{H}$ 318.1489, Found 318.1486.

***N*-(4-(Trifluoromethyl)benzyl)hexan-1-amine (3h)**

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), 4-trifluoromethylbenzylamine (175 mg, 1.0 mmol) and 1-hexamine (141 mg, 1.4 mmol) was stirred at 130 °C for 16 h. The product **3h** was isolated by a column chromatography on silica gel (*n*-hexanes/EtOAc = 100:1 to 10:1; 142 mg, 55%). TLC; R_f = 0.4 (20% EtOAc in hexanes). Data for **3h**: ^1H NMR (400 MHz, CDCl_3) δ 7.57 (d, J = 8.2 Hz, 2H), 7.44 (d, J = 8.2 Hz, 2H), 3.84 (s, 2H), 2.61 (t, J = 7.2 Hz, 2H), 1.58 (br s, 1H), 1.55–1.46 (m, 2H), 1.37–1.22 (m, 6H), 0.91–0.84 (m, 3H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 144.6, 129.1 (q, J_{CF} = 32.3 Hz), 128.3, 125.3 (q, J_{CF} = 3.8 Hz), 124.2 (q, J_{CF} = 272.0 Hz), 53.5, 49.5, 31.7, 30.0, 27.0, 22.6, 14.0; GC-MS for $\text{C}_{14}\text{H}_{20}\text{F}_3\text{N}$, m/z = 259 (M^+); HRMS (ESI-TOF) m/z : [$\text{M} + \text{H}$] $^+$ Calcd for $\text{C}_{14}\text{H}_{20}\text{F}_3\text{NH}$ 260.1621; Found 260.1627.

Ethyl 3-(benzylamino)propanoate (3i)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), β -alanine ethyl ester (117 mg, 1.0 mmol) and benzylamine (150 mg, 1.4 mmol) was stirred at 130 °C for 16 h. The product **3i** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 149 mg, 72%). TLC; R_f = 0.3 (20% EtOAc in hexanes). Data for **3i**: ^1H NMR (400 MHz, CDCl_3) δ 7.33–7.19 (m, 5H), 4.11 (q, J = 7.2 Hz, 2H), 3.78 (s, 2H), 2.87 (t, J = 6.5 Hz, 2H), 2.50 (t, J = 6.5 Hz, 2H), 1.82 (brs, 1H), 1.23 (t, J = 7.2 Hz, 3H), ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 172.7, 140.0, 128.3, 128.0, 126.8, 60.3, 53.7, 44.4, 34.7, 14.1 ppm; GC-MS for $\text{C}_{12}\text{H}_{17}\text{NO}_2$, m/z = 207 (M^+). ^1H and ^{13}C NMR spectral data were in good agreement with the literature values.³¹

4-Fluoro-*N*-hexylbenzenemethanamine (3j)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), 4-fluorobenzylamine (125 mg, 1.0 mmol) and 1-hexamine (141 mg, 1.4 mmol) was stirred at 130 °C for 16 h. The product **3j** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 132 mg, 63%). TLC; R_f = 0.3 (20% EtOAc in hexanes). Data for **3j**: ^1H NMR (400 MHz, CDCl_3) δ 7.30–7.24 (m, 2H), 7.02–6.95 (m, 2H), 3.74 (s, 2H), 2.59 (t, J = 7.3, 2H), 1.53–1.44 (m, 2H), 1.35–1.21 (m, 6H), 0.90–0.84 (m, 3H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 161.8 (d, J_{CF} = 244.6 Hz), 136.2 (d, J_{CF} = 3.1 Hz), 129.6 (d, J_{CF} = 7.9 Hz), 115.0 (d, J_{CF} = 21.2 Hz), 53.3, 49.4, 31.7, 30.0, 27.0, 22.6, 14.0 ppm; GC-MS for $\text{C}_{13}\text{H}_{20}\text{FN}$, m/z = 209 (M^+); HRMS (ESI-TOF) m/z : [$\text{M} + \text{H}$] $^+$ Calcd for $\text{C}_{13}\text{H}_{20}\text{FNH}$ 210.1653; Found 260.1654.

***N*-(4-fluorobenzyl)-*N*-(4-methoxybenzyl)amine (3k)**

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), 4-fluorobenzylamine (125 mg, 1.0 mmol) and 4-methoxybenzylamine (192 mg, 1.4 mmol) was stirred at 130 °C for 16 h. The product **3k** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 162 mg, 66%). TLC; R_f = 0.3 (20% EtOAc in hexanes). Data for **3k**: ^1H NMR (400 MHz, CDCl_3) δ 7.35–7.29 (m, 2H), 7.27 (d, J = 8.3 Hz, 2H), 7.06–6.99 (m, 2H), 6.90 (d, J = 8.3 Hz, 2H), 3.81 (s, 3H), 3.76 (s, 2H), 3.74 (s, 2H), 1.78 (br s, 1H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 161.8 (d, J_{CF} = 244.6 Hz), 158.5, 135.9 (d, J_{CF} = 3.1 Hz), 132.1, 129.6 (d, J_{CF} = 7.9 Hz), 129.2, 115.0

(d, $J_{\text{CF}} = 21.2$ Hz), 113.7, 55.1, 52.4, 52.1; GC-MS for $\text{C}_{15}\text{H}_{16}\text{FNO}$, $m/z = 245$ (M^+). ^1H and ^{13}C NMR spectral data were in good agreement with the literature values.³²

***N*-[(4-fluorophenyl)methyl]-4-methoxy-benzeneethanamine (3l)**

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), 4-fluorobenzylamine (125 mg, 1.0 mmol) and 4-methoxybenzeneethanamine (211 mg, 1.4 mmol) was stirred at 130 °C for 16 h. The product **3l** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 142 mg, 55%). TLC; $R_f = 0.3$ (20% EtOAc in hexanes). Data for **3l**: ^1H NMR (400 MHz, CDCl_3) δ 7.27–7.21 (m, 2H), 7.15–7.10 (m, 2H), 7.03–6.96 (m, 2H), 6.87–6.82 (m, 2H), 3.79 (s, 3H), 3.76 (s, 2H), 2.88–2.83 (m, 2H), 2.80–2.74 (m, 2H), 1.69 (br s, 1H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 161.8 (d, $J_{\text{CF}} = 244.6$ Hz), 157.9, 135.8 (d, $J_{\text{CF}} = 3.1$ Hz), 131.8, 129.5, 129.5 (d, $J_{\text{CF}} = 7.9$ Hz), 115.0 (d, $J_{\text{CF}} = 21.2$ Hz), 113.8, 55.1, 53.0, 50.6, 35.2 ppm; GC-MS for $\text{C}_{16}\text{H}_{18}\text{FNO}$, $m/z = 259$ (M^+); HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{16}\text{H}_{18}\text{FNOH}$ 260.1445; Found 260.1439.

***N*-[(4-Fluorophenyl)methyl]- β -methylbenzeneethanamine (3m)**

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), 4-fluorobenzylamine (125 mg, 1.0 mmol) and β -methylphenethylamine (189 mg, 1.4 mmol) was stirred at 130 °C for 16 h. The product **3m** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 141 mg, 58%). TLC; $R_f = 0.4$ (20% EtOAc in hexanes). Data for **3m**: ^1H NMR (400 MHz, CDCl_3) δ 7.37–7.30 (m, 2H), 7.26–7.19 (m, 5H), 7.03–6.96 (m, 2H), 3.74 (ABq, $J = 13.5$ Hz, 2H), 2.99 (qt, $J = 7.1$, 7.0 Hz, 1H), 2.84–2.77 (m, 2H), 1.55 (br s, 1H), 1.28 (d, $J = 7.0$ Hz, 3H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 161.7 (d, $J_{\text{CF}} = 244.2$ Hz), 145.1, 135.8 (d, $J_{\text{CF}} = 3.1$ Hz), 129.4 (d, $J_{\text{CF}} = 7.9$ Hz), 128.5, 127.1, 126.3, 115.0 (d, $J_{\text{CF}} = 21.2$ Hz), 56.1, 52.9, 39.9, 20.0 ppm; GC-MS for $\text{C}_{16}\text{H}_{18}\text{FN}$, $m/z = 243$ (M^+); HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{16}\text{H}_{18}\text{FNH}$ 244.1496; Found 244.1500.

4-Methoxy-*N*-(phenylmethyl)benzeneethanamine (3n)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), 4-methoxybenzeneethanamine (151 mg, 1.0 mmol) and benzylamine (150 mg, 1.4 mmol) was stirred at 130 °C for 16 h. The product **3n** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 169 mg, 70%). TLC; $R_f = 0.3$ (10% EtOAc in hexanes). Data for **3n**: ^1H NMR (400 MHz, CDCl_3) δ 7.37–7.23 (m, 5H), 7.15 (d, $J = 8.3$ Hz, 2H), 6.86 (d, $J = 8.3$ Hz, 2H), 3.82 (s, 2H), 3.80 (s, 3H), 2.89 (t, $J = 6.9$ Hz, 2H), 2.80 (t, $J = 6.9$ Hz, 2H), 1.66 (br s, 1H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 157.9, 140.1, 131.9, 129.5, 128.3, 128.0, 126.8, 113.8, 55.1, 53.8, 50.6, 35.3 ppm; GC-MS for $\text{C}_{16}\text{H}_{19}\text{NO}$, $m/z = 241$ (M^+). ^1H and ^{13}C NMR spectral data were in good agreement with the literature values.³³

***N*-(4-Methoxyphenethyl)hexan-1-amine (3o)**

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), 4-methoxybenzeneethanamine (151 mg, 1.0 mmol) and 1-hexamine (141 mg, 1.4 mmol)

was stirred at 130 °C for 16 h. The product **3o** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 119 mg, 51%). TLC; R_f = 0.3 (10% EtOAc in hexanes). Data for **3o**: ^1H NMR (400 MHz, CDCl_3) δ 7.12 (d, J = 8.7 Hz, 2H), 6.83 (d, J = 8.7 Hz, 2H), 3.78 (s, 3H), 2.86–2.81 (m, 2H), 2.78–2.72 (m, 2H), 2.62–2.57 (m, 2H), 1.68 (br s, 1H), 1.50–1.41 (m, 2H), 1.33–1.23 (m, 6H), 0.89–0.84 (m, 3H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 157.9, 132.0, 129.6, 113.8, 55.2, 51.4, 49.9, 35.3, 31.7, 29.9, 27.0, 22.6, 14.0 ppm; GC-MS for $\text{C}_{15}\text{H}_{25}\text{NO}$, m/z = 235 (M^+); HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{15}\text{H}_{25}\text{NOH}$ 236.2009; Found 236.2005.

***N*-Cyclohexyl-4-methoxybenzeneethanamine (3p)**

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), 4-methoxybenzeneethanamine (151 mg, 1.0 mmol) and cyclohexylamine (139 mg, 1.4 mmol) was stirred at 130 °C for 16 h. The product **3p** was isolated by a column chromatography on silica gel (*n*-hexanes/EtOAc = 100:1 to 10:1; 187 mg, 80%). TLC; R_f = 0.3 (20% EtOAc in hexanes). Data for **3p**: ^1H NMR (400 MHz, CDCl_3) δ 7.10 (d, J = 8.7 Hz, 2H), 6.81 (d, J = 8.7 Hz, 2H), 3.75 (s, 3H), 2.86–2.81 (m, 2H), 2.74–2.68 (m, 2H), 2.39 (tt, J = 10.6, 3.8 Hz, 1H), 1.88–1.78 (m, 2H), 1.74–1.64 (m, 2H), 1.62–1.54 (m, 1H), 1.48 (br s, 1H), 1.29–0.95 (m, 5H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 157.8, 132.0, 129.4, 113.7, 56.6, 55.0, 48.3, 35.5, 33.4, 26.0, 24.9 ppm; GC-MS for $\text{C}_{15}\text{H}_{23}\text{NO}$, m/z = 233 (M^+); HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{15}\text{H}_{23}\text{NOH}$ 234.1852; Found 234.1854.

***N*-(4-Methoxyphenethyl)-2,3-dihydro-1*H*-inden-2-amine (3q)**

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), 4-methoxybenzeneethanamine (151 mg, 1.0 mmol) and 2-aminoindane (186 mg, 1.4 mmol) was stirred at 130 °C for 16 h. The product **3q** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 144 mg, 54%). TLC; R_f = 0.3 (20% EtOAc in hexanes). Data for **3q**: ^1H NMR (400 MHz, CDCl_3) δ 7.22–7.12 (m, 6H), 6.89–6.83 (m, 2H), 3.80 (s, 3H), 3.65 (quintet, J = 7.0 Hz, 1H), 3.17 (dd, J = 7.2 Hz, 2H), 2.96–2.90 (m, 2H), 2.82–2.70 (m, 4H), 1.67 (br s, 1H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 158.0, 141.6, 131.9, 129.5, 126.3, 124.6, 113.9, 59.5, 55.2, 49.7, 39.9, 35.5 ppm; GC-MS for $\text{C}_{18}\text{H}_{21}\text{NO}$, m/z = 267 (M^+); HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{18}\text{H}_{21}\text{NOH}$ 268.1696; Found 268.1699.

***N*-(4-Methoxyphenethyl)-1-(4-methoxyphenyl)ethanamine (3r)**

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), 4-methoxybenzeneethanamine (151 mg, 1.0 mmol) and (*R*)-(+)-1-(4-methoxyphenyl)ethylamine (211 mg, 1.4 mmol) was stirred at 130 °C for 16 h. The product **3r** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 186 mg, 65%). TLC; R_f = 0.3 (20% EtOAc in hexanes). Data for **3r**: ^1H NMR (400 MHz, CDCl_3) δ 7.21–7.15 (m, 2H), 7.10–7.05 (m, 2H), 6.87–6.79 (m, 4H), 3.79 (s, 3H), 3.78 (s, 3H), 3.73 (q, J = 6.6 Hz, 1H), 2.79–2.60 (m, 4H), 1.86 (br s, 1H), 1.32 (d, J = 6.6, 3H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 158.3, 157.8, 137.4, 131.9, 129.4, 127.4, 113.7, 113.6, 57.4, 55.0, 48.9, 35.2, 24.1 ppm (one carbon signal obscured or overlapping); GC-MS for

$C_{18}H_{23}NO_2$, $m/z = 285$ (M^+); HRMS (ESI-TOF) m/z : $[M+H]^+$ Calcd for $C_{18}H_{23}NO_2H$ 286.1802; Found 286.1798.

***N*-(4-Methoxyphenethyl)-4-phenylbutan-2-amine (3s)**

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), 4-methoxybenzeneethanamine (151 mg, 1.0 mmol) and ($\pm$)-1-methyl-3-phenyl-1-propanamine (209 mg, 1.4 mmol) was stirred at 130 °C for 16 h. The product **3s** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 208 mg, 73%. TLC; $R_f = 0.3$ (20% EtOAc in hexanes). Data for **3s**: 1H NMR (400 MHz, $CDCl_3$) δ 7.30–7.25 (m, 2H), 7.21–7.11 (m, 5H), 6.88–6.83 (m, 2H), 3.79 (s, 3H), 2.94–2.84 (m, 1H), 2.82–2.70 (m, 3H), 2.70–2.52 (m, 3H), 1.82–1.72 (m, 1H), 1.66–1.56 (m, 1H), 1.54 (br s, 1H), 1.10 (d, $J = 6.3$ Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 157.9, 142.2, 132.0, 129.6, 128.3, 128.2, 125.6, 113.8, 55.2, 52.4, 48.5, 38.5, 35.5, 32.2, 20.2 ppm; GC-MS for $C_{19}H_{25}NO$, $m/z = 283$ (M^+); HRMS (ESI-TOF) m/z : $[M+H]^+$ Calcd for $C_{19}H_{25}NOH$ 284.2009; Found 284.2010.

4-Methoxy-*N*-[(4-methoxyphenyl)methyl]benzeneethanamine (3t)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), 4-methoxybenzeneethanamine (151 mg, 1.0 mmol) and 4-methoxybenzylamine (192 mg, 1.4 mmol) was stirred at 130 °C for 16 h. The product **3t** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 149 mg, 55%). TLC; $R_f = 0.3$ (20% EtOAc in hexanes). Data for **3t**: 1H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, $J = 8.3$ Hz, 2H), 7.13 (d, $J = 8.3$ Hz, 2H), 6.90–6.82 (m, 4H), 3.80 (s, 3H), 3.79 (s, 3H), 3.75 (s, 2H), 2.87 (t, $J = 7.1$ Hz, 2H), 2.78 (t, $J = 7.1$ Hz, 2H), 1.71 (br s, 1H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 158.5, 157.9, 132.3, 131.9, 129.5, 129.2, 113.7, 113.6, 55.1, 55.1, 53.2, 50.6, 35.2 ppm; GC-MS for $C_{17}H_{21}NO_2$, $m/z = 271$ (M^+). 1H and ^{13}C NMR spectral data were in good agreement with the literature values.³³

***N*-(3-Fluorophenethyl)-2,3-dihydro-1*H*-inden-2-amine (3u)**

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), 2-(3-fluorophenyl)ethylamine (139 mg, 1.0 mmol) and 2-aminoindane (186 mg, 1.4 mmol) was stirred at 130 °C for 16 h. The product **3u** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 193 mg, 76%). TLC; $R_f = 0.4$ (10% EtOAc in hexanes). Data for **3u**: 1H NMR (400 MHz, $CDCl_3$) δ 7.3–7.24 (m, 1H), 7.24–7.12 (m, 4H), 7.06–7.00 (m, 1H), 6.99–6.89 (m, 2H), 3.67 (quintet, $J = 6.9$ Hz, 1H), 3.18 (dd, $J = 15.5, 7.2$ Hz, 2H), 3.01–2.92 (m, 2H), 2.89–2.81 (m, 2H), 2.75 (dd, $J = 15.5, 6.6$ Hz, 2H), 1.63 (br s, 1H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.8 (d, $J_{CF} = 245.5$ Hz), 142.5 (d, $J_{CF} = 7.2$ Hz), 141.5, 129.8 (d, $J_{CF} = 8.3$ Hz), 126.4, 124.6, 124.3 (d, $J_{CF} = 2.7$ Hz), 115.4 (d, $J_{CF} = 20.8$ Hz), 113.0 (d, $J_{CF} = 21.0$ Hz), 59.4, 49.2, 39.9, 36.2 (d, $J_{CF} = 1.6$ Hz) ppm; GC-MS for $C_{17}H_{18}FN$, $m/z = 255$ (M^+); HRMS (ESI-TOF) m/z : $[M+H]^+$ Calcd for $C_{17}H_{18}FNH$ 256.1496; Found 256.1501.

***N*-(3-Fluorophenethyl)-1-(4-methoxyphenyl)ethanamine (3v)**

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), 2-(3-fluorophenyl)ethylamine (139 mg, 1.0 mmol) and (*R*)-(+)-1-(4-methoxyphenyl)ethylamine (211 mg, 1.4 mmol) was stirred at 130 °C for 16 h. The product **3v** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 157 mg, 58%). TLC; R_f = 0.3 (20% EtOAc in hexanes). Data for **3v**: ^1H NMR (400 MHz, CDCl_3) δ 7.27–7.16 (m, 3H), 6.98–6.80 (m, 5H), 3.80 (s, 3H), 3.73 (q, J = 6.6 Hz, 1H), 2.83–2.63 (m, 4H), 1.60 (br s, 1H), 1.32 (d, J = 6.6 Hz, 3H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 162.8 (d, J_{CF} = 245.4 Hz), 158.5, 142.6 (d, J_{CF} = 7.2 Hz), 137.3, 129.7 (d, J_{CF} = 8.3 Hz), 127.5, 124.3 (d, J_{CF} = 2.7 Hz), 115.4 (d, J_{CF} = 20.9 Hz), 113.7, 112.9 (d, J_{CF} = 21.0 Hz), 57.5, 55.2, 48.5, 36.1 (d, J_{CF} = 1.7 Hz), 24.2 ppm; GC-MS for $\text{C}_{17}\text{H}_{20}\text{FNO}$, m/z = 273 (M^+); HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{17}\text{H}_{20}\text{FNOH}$ 274.1602; Found 274.1604.

***N*-Cyclohexyl-1,3-benzodioxole-5-methanamine (3w)**

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), 1-(1,3-benzodioxol-5-yl)methanamine (151 mg, 1.0 mmol) and cyclohexylamine (139 mg, 1.4 mmol) was stirred at 130 °C for 16 h. The product **3w** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 138 mg, 59%). TLC; R_f = 0.3 (20% EtOAc in hexanes). Data for **3w**: ^1H NMR (400 MHz, CDCl_3) δ 6.83–6.81 (m, 1H), 6.75–6.73 (m, 2H), 5.92 (s, 2H), 3.70 (s, 2H), 2.45 (tt, J = 10.4, 3.8 Hz, 1H), 1.95–1.84 (m, 2H), 1.77–1.67 (m, 2H), 1.64–1.54 (m, 1H), 1.30–1.04 (m, 5H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 147.6, 146.3, 134.8, 121.1, 108.6, 108.0, 100.8, 55.9, 50.7, 33.4, 26.1, 24.9 ppm; GC-MS for $\text{C}_{14}\text{H}_{19}\text{NO}_2$, m/z = 233 (M^+). ^1H and ^{13}C NMR spectral data were in good agreement with the literature values.³⁴

***N*-(Benzo[d][1,3]dioxol-5-ylmethyl)-1-(4-methoxyphenyl)ethanamine (3x)**

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), 1-(1,3-benzodioxol-5-yl)methanamine (151 mg, 1.0 mmol) and (*R*)-(+)-1-(4-methoxyphenyl)ethylamine (211 mg, 1.4 mmol) was stirred at 130 °C for 16 h. The product **3x** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 171 mg, 60%). TLC; R_f = 0.3 (20% EtOAc in hexanes). Data for **3x**: ^1H NMR (400 MHz, CDCl_3) δ 7.30–7.24 (m, 2H), 6.93–6.86 (m, 2H), 6.82–6.78 (m, 1H), 6.77–6.67 (m, 2H), 5.93 (s, 2H), 3.82 (s, 3H), 3.76 (q, J = 6.6 Hz, 1H), 3.52 (ABq, J = 13.2 Hz, 2H), 1.70 (br s, 1H), 1.34 (d, J = 6.6 Hz, 3H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 158.5, 147.6, 146.3, 137.4, 134.5, 127.7, 121.1, 113.8, 108.7, 108.0, 100.8, 56.5, 55.2, 51.3, 24.4 ppm; GC-MS for $\text{C}_{17}\text{H}_{19}\text{NO}_3$, m/z = 285 (M^+); HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{17}\text{H}_{19}\text{NO}_3\text{H}$ 286.1438; Found 286.1427.

***N*-(Benzo[d][1,3]dioxol-5-ylmethyl)-2-(4-methoxyphenyl)propan-1-amine (3y)**

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), 1-(1,3-benzodioxol-5-yl)methanamine (151 mg, 1.0 mmol) and ($\pm$)-1-(4-methoxyphenyl)ethylamine (211 mg, 1.4 mmol) was stirred at 130 °C for 16 h. The product **3y** was isolated by a column chromatography on silica gel (*n*-hexanes/EtOAc = 100:1 to 10:1; 152 mg, 56%). TLC; R_f = 0.3 (20% EtOAc in hexanes). Data for **3y**: ^1H NMR (400

MHz, CDCl₃) δ 7.35–7.28 (m, 2H), 7.24–7.18 (m, 3H), 6.75 (d, J = 1.6 Hz, 2H), 6.73 (d, J = 7.9 Hz, 1H), 6.68 (dd, J = 7.9, 1.6 Hz, 1H), 5.93 (s, 2H), 3.66 (ABq, J = 13.2 Hz, 2H), 2.96 (sextet, J = 7.1 Hz, 1H), 2.77 (d, J = 7.2 Hz, 2H), 1.66 (br s, 1H), 1.26 (d, J = 7.1 Hz, 3H) ppm; ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 147.6, 146.4, 145.2, 134.1, 128.5, 127.2, 126.4, 121.1, 108.6, 108.0, 100.8, 56.0, 53.5, 39.9, 20.1 ppm; GC-MS for C₁₇H₁₉NO₂, m/z = 269 (M⁺); HRMS (ESI-TOF) m/z : [M+H]⁺ Calcd for C₁₇H₁₉NO₂H 270.1489; Found 270.1463.

N-Hexyl-1,2,3,4-tetrahydro-1-naphthalenamine (3z)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), 1,2,3,4-tetrahydro-1-naphthalenamine (147 mg, 1.0 mmol) 1-hexamine (141 mg, 1.4 mmol) was stirred at 130 °C for 16 h. The product **3z** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 106 mg, 46%). TLC; R_f = 0.3 (10% EtOAc in hexanes). Data for **3z**: ¹H NMR (400 MHz, CDCl₃) δ 7.37–7.30 (m, 1H), 7.21–7.05 (m, 3H), 3.77 (t, J = 4.8 Hz, 1H), 2.87–2.61 (m, 1H), 2.03–1.91 (m, 1H), 1.91–1.81 (m, 2H), 1.78–1.68 (m, 1H), 1.56–1.46 (m, 2H), 1.41–1.19 (m, 7H), 0.94–0.85 (m, 3H) ppm; ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 139.3, 137.3, 129.0, 128.7, 126.5, 125.6, 55.4, 47.3, 31.8, 30.4, 29.3, 28.2, 27.1, 22.6, 18.9, 14.1 ppm; GC-MS for C₁₆H₂₅N, m/z = 231 (M⁺); HRMS (ESI-TOF) m/z : [M+H]⁺ Calcd for C₁₆H₂₅NH 232.2060; Found 232.2053.

N-[2-(4-Methoxyphenyl)ethyl]-1,2,3,4-tetrahydro-1-naphthalenamine (3aa)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), 1,2,3,4-tetrahydro-1-naphthalenamine (147 mg, 1.0 mmol) and 4-methoxybenzeneethanamine (211 mg, 1.4 mmol) was stirred at 130 °C for 16 h. The product **3aa** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 177 mg, 63%). TLC; R_f = 0.3 (10% EtOAc in hexanes). Data for **3aa**: ¹H NMR (400 MHz, CDCl₃) δ 7.28–7.23 (m, 1H), 7.21–7.13 (m, 4H), 7.12–7.07 (m, 1H), 6.90–6.85 (m, 2H), 3.82 (s, 3H), 3.81 (t, J = 4.7 Hz, 1H), 3.05–2.89 (m, 2H), 2.87–2.69 (m, 4H), 2.01–1.86 (m, 3H), 1.80–1.70 (m, 1H), 1.63 (br s, 1H) ppm; ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 157.9, 139.0, 137.3, 132.1, 129.6, 129.0, 128.5, 126.5, 125.6, 113.7, 55.3, 55.2, 48.6, 35.7, 29.3, 28.2, 19.0 ppm; GC-MS for C₁₉H₂₃NO, m/z = 281 (M⁺); HRMS (ESI-TOF) m/z : [M+H]⁺ Calcd for C₁₉H₂₃NOH 282.1852; Found 282.1843.

N-Cyclohexyl-5-methoxytryptamine (3bb)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), 5-methoxytryptamine (190 mg, 1.0 mmol) and cyclohexylamine (139 mg, 1.4 mmol) was stirred at 130 °C for 16 h. The product **3bb** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 218 mg, 80%). TLC; R_f = 0.2 (30% EtOAc in hexanes). Data for **3bb**: ¹H NMR (400 MHz, CDCl₃) δ 8.21 (br s, 1H), 7.26–7.20 (m, 1H), 7.08–7.05 (m, 1H), 7.02–6.99 (m, 1H), 6.85 (dd, J = 8.8, 2.5 Hz, 1H), 3.86 (s, 3H), 3.07–2.90 (m, 4H), 2.45 (tt, J = 10.5, 3.7 Hz, 1H), 1.91–1.78 (m, 3H), 1.75–1.65 (m, 2H), 1.64–1.55 (m, 1H), 1.29–0.99 (m, 5H) ppm; ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 153.8, 131.5, 127.8, 122.8, 113.6, 112.1, 111.8, 100.6, 56.8, 55.9, 46.8, 33.5, 26.1, 25.9, 25.0 ppm; GC-MS for C₁₇H₂₄N₂O, m/z = 272 (M⁺); HRMS (ESI-TOF) m/z : [M+H]⁺ Calcd for C₁₇H₂₄FN₂OH 273.1961; Found 273.1960.

N-Cyclohexyl-2-furanmethanamine (3cc)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), 2-(2-aminoethyl)furan (97 mg, 1.0 mmol) and cyclohexylamine (139 mg, 1.4 mmol) was stirred at 130 °C for 16 h. The product **3cc** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 124 mg, 69%). TLC; R_f = 0.3 (10% EtOAc in hexanes). Data for **3cc**: ^1H NMR (400 MHz, CDCl_3) δ 7.32 (dd, J = 1.9, 0.9 Hz, 1H), 6.28 (dd, J = 3.2, 1.9 Hz, 1H), 6.14–6.12 (m, 1H), 3.78 (s, 2H), 2.42 (tt, J = 10.4, 3.8, Hz, 1H), 1.90–1.81 (m, 2H), 1.74–1.66 (m, 2H), 1.63–1.46 (m, 2H), 1.28–1.02 (m, 5H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 154.2, 141.5, 110.0, 106.4, 55.7, 43.2, 33.2, 26.0, 24.9 ppm; GC-MS for $\text{C}_{11}\text{H}_{17}\text{NO}$, m/z = 179 (M^+). ^1H and ^{13}C NMR spectral data were in good agreement with the literature values.³⁵

4-[2-Cyclohexylaminoethyl]phenol (3dd)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), tyramine (136 mg, 1.0 mmol) and cyclohexylamine (139 mg, 1.4 mmol) was stirred at 130 °C for 16 h. The product **3dd** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 152 mg, 69%). TLC; R_f = 0.3 (20% EtOAc in hexanes). Data for **3dd**: ^1H NMR (400 MHz, CDCl_3) δ 7.02 (d, J = 8.3 Hz, 2H), 6.72 (d, J = 8.3 Hz, 2H), 4.71 (br s, 1H), 2.93 (t, J = 6.9 Hz, 2H), 2.75 (t, J = 6.9 Hz, 2H), 2.47 (tt, J = 10.6, 3.6 Hz, 1H), 1.92–1.85 (m, 2H), 1.75–1.66 (m, 2H), 1.64–1.55 (m, 1H), 1.28–1.08 (m, 5H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 155.5, 130.0, 129.7, 115.9, 56.9, 47.6, 34.7, 32.9, 25.9, 25.0 ppm; GC-MS for $\text{C}_{14}\text{H}_{21}\text{NO}$, m/z = 219 (M^+); Anal. Calcd for $\text{C}_{14}\text{H}_{21}\text{NO}$: C, 76.67; H, 9.65. Found: C, 76.78; H, 9.35; HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{14}\text{H}_{21}\text{NOH}$ 220.1696; Found 220.1698.

Dibenzylamine (4a)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %) and benzylamine (107 mg, 1.0 mmol) was stirred at 130 °C for 16 h. The product **4a** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 88 mg, 89%). TLC; R_f = 0.3 (10% EtOAc in hexanes). Data for **4a**: ^1H NMR (400 MHz, CDCl_3) δ 7.42–7.24 (m, 10H), 3.84 (s, 4H), 2.08 (br s, 1H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 140.0, 128.4, 128.1, 126.9, 53.0 ppm; GC-MS for $\text{C}_{14}\text{H}_{15}\text{N}$, m/z = 197 (M^+). ^1H and ^{13}C NMR spectral data were in good agreement with the literature values.³⁶

Bis(4-methylbenzyl)amine (4b)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %) and 4-methylbenzylamine (121 mg, 1.0 mmol) was stirred at 130 °C for 16 h. The product **4b** was isolated by a column chromatography on silica gel (*n*-hexane/ethyl acetate = 100:1 to 10:1; 106 mg, 94%). TLC; R_f = 0.4 (20% EtOAc in hexanes). Data for **4b**: ^1H NMR (400 MHz, CDCl_3) δ 7.27 (d, J = 7.9 Hz, 4H), 7.18 (d, J = 7.9 Hz, 4H), 3.80 (s, 4H), 2.38 (s, 6H), 1.70 (br s, 1H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 137.2, 136.4, 129.0, 128.1, 52.7, 21.1 ppm; GC-MS for $\text{C}_{16}\text{H}_{19}\text{N}$, m/z = 225 (M^+). ^1H and ^{13}C NMR spectral data were in good agreement with the literature values.^{36,37}

Bis(4-methoxybenzyl)amine (4c)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %) and 4-methoxybenzylamine (137 mg, 1.0 mmol) was stirred at 130 °C for 16 h. The product **4c** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 111 mg, 86%). TLC; R_f = 0.3 (10% EtOAc in hexanes). Data for **4c** ^1H NMR (400 MHz, CDCl_3) δ 7.29–7.24 (m, 4H), 6.91–6.86 (m, 4H), 3.81 (s, 6H), 3.74 (s, 4H), 1.69 (br s, 1H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 158.5, 132.4, 129.2, 113.6, 55.1, 52.3 ppm; GC-MS for $\text{C}_{16}\text{H}_{19}\text{NO}_2$, m/z = 257 (M^+). ^1H and ^{13}C NMR spectral data were in good agreement with the literature values.^{36,37}

***N,N*-Bis(4-chlorobenzyl)amine (4d)**

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %) and 4-chlorobenzylamine (141 mg, 1.0 mmol) was stirred at 130 °C for 16 h. The product **4d** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 122 mg, 92%). TLC; R_f = 0.5 (10% EtOAc in hexanes). Data for **4d** ^1H NMR (400 MHz, CDCl_3) δ 7.33–7.28 (m, 8H), 3.76 (s, 4H), 1.64 (br s, 1H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 138.5, 132.6, 129.4, 128.5, 52.2 ppm; GC-MS for $\text{C}_{14}\text{H}_{13}\text{Cl}_2\text{N}$, m/z = 265 (M^+). ^1H and ^{13}C NMR spectral data were in good agreement with the literature values.^{37,38}

***N*-([1,1'-Biphenyl]-4-ylmethyl)-[1,1'-biphenyl]-4-methanamine (4e)**

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %) and 4-phenylbenzylamine (183 mg, 1.0 mmol) was stirred at 130 °C for 16 h. The product **4e** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 148 mg, 85%). TLC; R_f = 0.5 (20% EtOAc in hexanes). Data for **4e** ^1H NMR (400 MHz, CDCl_3) δ 7.59 (t, J = 8.4 Hz, 8H), 7.49–7.42 (m, 8H), 7.34 (t, J = 7.6 Hz, 2H), 3.90 (s, 4H), 1.65 (br s, 1H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 140.9, 139.9, 139.4, 128.7, 128.6, 127.1, 127.0, 52.8 ppm (one carbon signal obscured or overlapping); GC-MS for $\text{C}_{26}\text{H}_{23}\text{N}$, m/z = 349 (M^+). ^1H and ^{13}C NMR spectral data were in good agreement with the literature values.³⁹

4-Fluoro-*N*-[(4-fluorophenyl)methyl]benzenemethanamine (4f)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %) and 4-phenylbenzylamine (125 mg, 1.0 mmol) was stirred at 130 °C for 16 h. The product **4f** was isolated by a column chromatography on silica gel (*n*-hexanes/EtOAc = 100:1 to 10:1; 106 mg, 91%). TLC; R_f = 0.4 (20% EtOAc in hexanes). Data for **4f** ^1H NMR (400 MHz, CDCl_3) δ 7.36–7.28 (m, 4H), 7.07–6.99 (m, 4H), 3.78 (s, 4H), 1.67 (br s, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 161.8 (d, J_{CF} = 244.5 Hz), 135.8 (d, J_{CF} = 3.1 Hz), 129.6 (d, J_{CF} = 8.0 Hz), 115.1 (d, J_{CF} = 21.3 Hz), 52.3 ppm; GC-MS for $\text{C}_{14}\text{H}_{13}\text{F}_2\text{N}$, m/z = 233 (M^+). ^1H and ^{13}C NMR spectral data were in good agreement with the literature values.³⁸

4-(Trifluoromethyl)-*N*-[[4-(trifluoromethyl)phenyl]methyl]benzenemethanamine (4g)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %) and 4-(trifluoromethyl)benzenemethanamine (175 mg, 1.0 mmol) was stirred at 130 °C

for 16 h. The product **4g** was isolated by a column chromatography on silica gel (*n*-hexanes/EtOAc = 100:1 to 10:1; 140 mg, 84%). TLC; R_f = 0.5 (20% EtOAc in hexanes). Data for **4g** ^1H NMR (400 MHz, CDCl_3) δ 7.64–7.57 (m, 4H), 7.51–7.46 (m, 4H), 3.88 (s, 4H), 1.75 (br s, 1H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 144.1, 129.4 (q, J_{CF} = 32.4 Hz), 128.3, 125.3 (q, J_{CF} = 3.8 Hz), 124.2 (q, J_{CF} = 271.8 Hz), 52.6 ppm; GC-MS for $\text{C}_{16}\text{H}_{13}\text{F}_6\text{N}$, m/z = 333 (M^+). ^1H and ^{13}C NMR spectral data were in good agreement with the literature values.^{38,40}

Bis(3-methoxybenzyl)amine (4h)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %) and 3-methoxybenzylamine (137 mg, 1.0 mmol) was stirred at 130 °C for 16 h. The product **4h** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 108 mg, 84%). TLC; R_f = 0.3 (10% EtOAc in hexanes). Data for **4h** ^1H NMR (400 MHz, CDCl_3) δ 7.29–7.22 (m, 2H), 6.97–6.91 (m, 4H), 6.84–6.78 (m, 2H), 3.82 (s, 6H), 3.80 (s, 4H), 1.71 (br s, 1H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 159.6, 141.9, 129.3, 120.4, 113.5, 112.4, 55.1, 53.0 ppm; GC-MS for $\text{C}_{16}\text{H}_{19}\text{NO}_2$, m/z = 257 (M^+). ^1H and ^{13}C NMR spectral data were in good agreement with the literature values.³⁶

N,N-Bis(3-chlorobenzyl)amine (4i)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %) and 3-chlorobenzylamine (141 mg, 1.0 mmol) was stirred at 130 °C for 16 h. The product **4i** was isolated by a column chromatography on silica gel (*n*-hexanes/EtOAc = 100:1 to 10:1; 118 mg, 89%). TLC; R_f = 0.3 (10% EtOAc in hexanes). Data for **4i** ^1H NMR (400 MHz, CDCl_3) δ 7.37–7.34 (m, 2H), 7.29–7.19 (m, 6H), 3.77 (s, 4H), 1.65 (br s, 1H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 142.1, 134.2, 129.6, 128.1, 127.2, 126.2, 52.5 ppm; GC-MS for $\text{C}_{14}\text{H}_{13}\text{Cl}_2\text{N}$, m/z = 265 (M^+). ^1H and ^{13}C NMR spectral data were in good agreement with the literature values.⁴¹

Bis(3,4-methylenedioxybenzyl)amine (4j)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %) and 1-(1,3-benzodioxol-5-yl)methanamine (151 mg, 1.0 mmol) was stirred at 130 °C for 16 h. The product **4j** was isolated by a column chromatography on silica gel (*n*-hexanes/EtOAc = 100:1 to 10:1; 110 mg, 77%). TLC; R_f = 0.4 (40% EtOAc in hexanes). Data for **4j** ^1H NMR (400 MHz, CDCl_3) δ 6.85 (s, 2H), 6.77–6.75 (m, 4H), 5.94 (s, 4H), 3.69 (s, 4H), 1.59 (br s, 1H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 147.7, 146.5, 134.3, 121.2, 108.7, 108.0, 100.9, 52.7 ppm; GC-MS for $\text{C}_{16}\text{H}_{15}\text{NO}_4$, m/z = 285 (M^+); HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{16}\text{H}_{15}\text{NO}_4\text{H}$ 286.1074; Found 286.1070.

Bis(3,4,5-trimethoxybenzyl)amine (4k)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %) and 3,4,5-trimethoxybenzylamine (197 mg, 1.0 mmol) was stirred at 130 °C for 16 h. The product **4k** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 115 mg, 61%). TLC; R_f = 0.3 (50% EtOAc in hexanes). Data for **4k** ^1H NMR (400 MHz, CDCl_3) δ 6.56 (s, 4H), 3.84 (s, 12H), 3.81 (s, 6H), 3.74 (s, 4H), 1.80 (br s, 1H)

ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 153.1, 136.6, 135.8, 104.7, 60.7, 55.9, 53.3 ppm; GC-MS for $\text{C}_{20}\text{H}_{27}\text{NO}_6$, m/z = 377 (M^+); HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{20}\text{H}_{27}\text{NO}_6$ 378.1911; Found 378.1892.

4-Methoxy-*N*-[(1*R*)-1-(4-methoxyphenyl)ethyl]- α -methyl-(α *R*)-benzenemethanamine (**4l**)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %) and (*R*)-(+)-1-(4-methoxyphenyl)ethylamine (151 mg, 1.0 mmol) was stirred at 130 °C for 16 h. The product **4l** was isolated by a column chromatography on silica gel (*n*-hexanes/EtOAc = 100:1 to 10:1; 107 mg, 75%), 7:1 mixture of diastereomers, = -211.1 (c = 0.12 in CH_2Cl_2); TLC; R_f = 0.3 (20% EtOAc in hexanes). Data for **4l** ^1H NMR (400 MHz, CDCl_3) δ 7.13 (d, J = 8.6 Hz, 4H), 6.89–6.84 (m, 4H), 3.82 (s, 6H), 3.45 (q, J = 6.7 Hz, 2H), 1.54 (br s, 1H), 1.25 (d, J = 6.7 Hz, 6H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 158.4, 137.7, 127.6, 113.7, 55.2, 54.2, 24.9 ppm; GC-MS for $\text{C}_{18}\text{H}_{23}\text{NO}_2$, m/z = 285 (M^+). ^1H and ^{13}C NMR spectral data were in good agreement with the literature values.⁴²

4-Methoxy-*N*-[2-(4-methoxyphenyl)ethyl]benzeneethanamine (**4m**)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %) and 4-methoxybenzeneethanamine (151 mg, 1.0 mmol) was stirred at 130 °C for 16 h. The product **4m** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 127 mg, 89%). TLC; R_f = 0.3 (10% EtOAc in hexanes). Data for **4m** ^1H NMR (400 MHz, CDCl_3) δ 7.10–7.05 (m, 4H), 6.84–6.79 (m, 4H), 3.79 (s, 6H), 2.88–2.82 (m, 4H), 2.76–2.70 (m, 4H), 1.56 (br s, 1H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 157.9, 131.9, 129.5, 113.8, 55.2, 51.2, 35.3 ppm; GC-MS for $\text{C}_{18}\text{H}_{23}\text{NO}_2$, m/z = 285 (M^+); HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{18}\text{H}_{23}\text{NO}_2$ 286.1802; Found 286.1800.

3-Methoxy-*N*-[2-(3-methoxyphenyl)ethyl]benzeneethanamine (**4n**)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %) and 3-methoxybenzeneethanamine (139 mg, 1.0 mmol) was stirred at 130 °C for 16 h. The product **4n** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1). Isolated yield: 128 mg, 90%. TLC; R_f = 0.3 (10% EtOAc in hexanes). Data for **4n** ^1H NMR (400 MHz, CDCl_3) δ 7.23–7.16 (m, 2H), 6.80–6.71 (m, 6H), 3.79 (s, 6H), 2.91 (t, J = 7.2 Hz, 4H), 2.79 (t, J = 7.2 Hz, 4H), 1.91 (br s, 1H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 159.6, 141.4, 129.4, 121.0, 114.3, 111.5, 55.1, 50.9, 36.2 ppm; GC-MS for $\text{C}_{18}\text{H}_{23}\text{NO}_2$, m/z = 285 (M^+); HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{18}\text{H}_{23}\text{NO}_2$ 286.1802; Found 286.1798.

3-Fluoro-*N*-[2-(3-fluorophenyl)ethyl]benzeneethanamine (**4o**)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %) and 3-fluorobenzeneethanamine (139 mg, 1.0 mmol) was stirred at 130 °C for 16 h. The product **4o** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 114 mg, 87%). TLC; R_f = 0.4 (10% EtOAc in hexanes). Data for **4o** ^1H NMR (400 MHz, CDCl_3) δ 7.26–7.18 (m, 2H), 6.98–6.83 (m, 6H), 2.93–2.86 (m, 4H), 2.82–2.76 (m, 4H), 1.68 (br s, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 162.9 (d, J_{CF} = 245.7 Hz), 142.3 (d, J_{CF} = 7.1 Hz), 129.9 (d, J_{CF} = 8.3 Hz), 124.3 (d, J_{CF} = 2.8 Hz), 115.4 (d, J_{CF} = 20.9 Hz),

113.1 (d, $J_{\text{CF}} = 21.0$ Hz), 50.6, 35.9 (d, $J_{\text{CF}} = 1.4$ Hz) ppm; GC-MS for $\text{C}_{16}\text{H}_{17}\text{F}_2\text{N}$, $m/z = 261$ (M^+); HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{16}\text{H}_{17}\text{F}_2\text{NH}$ 262.1402; Found 262.1389.

β -Methyl-*N*-(2-phenylpropyl)benzeneethanamine (4p)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %) and (R)-(+)- β -methylphenethylamine (135 mg, 1.0 mmol) was stirred at 130 °C for 16 h. The product **4p** was isolated by a column chromatography on silica gel (*n*-hexane/ethyl acetate = 100:1 to 10:1; 118 mg, 93%), 1.15:1 mixture of diastereomers. TLC; $R_f = 0.5$ (30% EtOAc in hexanes). Data for **4p** ^1H NMR (400 MHz, CDCl_3) δ 7.26–7.21 (m, 4H), 7.20–7.14 (m, 2H), 7.13–7.07 (m, 4H), 2.95–2.84 (m, 2H), 2.84–2.66 (m, 4H), 1.49 (br s, 1H), 1.21–1.17 (2d, $J = 6.9$ Hz, 6H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 145.1, 128.5, 127.0, 126.2, 56.7, 39.5, 19.8 ppm; GC-MS for $\text{C}_{18}\text{H}_{23}\text{N}$, $m/z = 253$ (M^+). ^1H and ^{13}C NMR spectral data were in good agreement with the literature values.⁴³

α -Methyl-*N*-(1-methyl-3-phenylpropyl)benzenepropanamine (4q)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %) and α -methylbenzenepropanamine (149 mg, 1.0 mmol) was stirred at 130 °C for 16 h. The product **4q** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 126 mg, 90%), 1:1 mixture of diastereomers. TLC; $R_f = 0.5$ (40% EtOAc in hexanes). Data for **4q** ^1H NMR (400 MHz, CDCl_3) δ 7.58–6.97 (m, 10H), 2.85–2.74 (m, 2H), 2.73–2.58 (m, 4H), 1.84–1.70 (m, 2H), 1.69–1.57 (m, 2H), 1.15–1.04 (m, 6H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 142.4 (isomers 1 and 2), 128.3 (isomers 1 and 2), 128.2 (isomers 1 and 2), 125.6 (isomers 1 and 2), 49.4 (isomer 1), 49.2 (isomer 2), 39.3 (isomer 1), 38.8 (isomer 2), 32.4 (isomer 1), 32.2 (isomer 2), 21.1 (isomer 1), 20.7 (isomer 2) ppm; GC-MS for $\text{C}_{20}\text{H}_{27}\text{N}$, $m/z = 281$ (M^+). ^1H and ^{13}C NMR spectral data were in good agreement with the literature values.⁴⁴

Di-[2-aminoindane] (4r)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %) and 2-indanamine (133 mg, 1.0 mmol) was stirred at 130 °C for 16 h. The product **4r** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 91 mg, 73%). TLC; $R_f = 0.5$ (20% EtOAc in hexanes). Data for **4r** ^1H NMR (400 MHz, CDCl_3) δ 7.30–7.24 (m, 4H), 7.24–7.18 (m, 4H), 3.83 (quintet, $J = 7.2$ Hz, 2H), 3.26 (dd, $J = 15.4$, 7.2 Hz, 4H), 2.85 (dd, $J = 15.4$, 7.2 Hz, 4H), 1.77 (br s, 1H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 141.5, 126.3, 124.5, 58.1, 40.2 ppm; GC-MS for $\text{C}_{18}\text{H}_{19}\text{N}$, $m/z = 249$ (M^+); HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{18}\text{H}_{19}\text{NH}$ 250.1590; Found 250.1598.

Bis(cyclohexyl)amine (4s)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %) and cyclohexylamine (99 mg, 1.0 mmol) was stirred at 130 °C for 16 h. The product **4s** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 86 mg, 95%). TLC; $R_f = 0.3$ (20% EtOAc in hexanes). Data for **4s** ^1H NMR (400 MHz, CDCl_3) δ 2.47 (tt, $J = 10.6$, 3.7 Hz, 2H), 1.82–1.74 (m, 4H), 1.68–1.59 (m, 4H), 1.57–1.49 (m, 2H),

1.24–0.88 (m, 10H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 52.8, 34.1, 26.0, 25.1 ppm; GC-MS for $\text{C}_{12}\text{H}_{23}\text{N}$, $m/z = 181$ (M^+). ^1H and ^{13}C NMR spectral data were in good agreement with the literature values.^{45,46}

***N*-(2-Thienylethyl)-2-thiopheneethanamine (4t)**

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %) and 2-thiopheneethanamine (127 mg, 1.0 mmol) was stirred at 130 °C for 16 h. The product **4t** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 106 mg, 89%). TLC; $R_f = 0.4$ (30% EtOAc in hexanes). Data for **4t**: ^1H NMR (400 MHz, CDCl_3) δ 7.22–7.04 (m, 2H), 6.96–6.87 (m, 2H), 6.85–6.75 (m, 2H), 3.06–2.99 (m, 4H), 2.98–2.90 (m, 4H), 2.45 (br s, 1H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 142.2, 126.8, 125.0, 123.5, 50.7, 30.2 ppm; GC-MS for $\text{C}_{12}\text{H}_{15}\text{NS}_2$, $m/z = 237$ (M^+); HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{12}\text{H}_{15}\text{NS}_2\text{H}$ 238.0719; Found 238.0716.

Di-*n*-hexylamine (4u)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %) and 1-hexamine (101 mg, 1.0 mmol) was stirred at 130 °C for 16 h. The product **4u** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 40 mg, 43%). TLC; $R_f = 0.3$ (30% EtOAc in hexanes). Data for **4u**: ^1H NMR (400 MHz, CDCl_3) δ 2.59 (t, $J = 7.4$, 4H), 2.24 (br s, 1H), 1.54–1.44 (m, 4H), 1.35–1.19 (m, 12H), 0.90–0.82 (m, 6H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 50.0, 31.7, 29.8, 27.1, 22.6, 14.0 ppm; GC-MS for $\text{C}_{12}\text{H}_{27}\text{N}$, $m/z = 185$ (M^+). ^1H and ^{13}C NMR spectral data were in good agreement with the literature values.^{46,47}

***N,N*-Dibutylamine (4v)**

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %) and *n*-butylamine (73 mg, 1.0 mmol) was stirred at 130 °C for 16 h. The product **4v** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 30 mg, 46%). TLC; $R_f = 0.3$ (30% EtOAc in hexanes). Data for **4v**: ^1H NMR (400 MHz, CDCl_3) δ 2.43 (t, $J = 7.2$ Hz, 4H), 1.37–1.25 (m, 4H), 1.24–1.11 (m, 4H), 0.86 (br s, 1H), 0.75 (t, $J = 7.3$ Hz, 6H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 49.6, 32.1, 20.2, 13.7 ppm; GC-MS for $\text{C}_8\text{H}_{19}\text{N}$, $m/z = 129$ (M^+). ^1H and ^{13}C NMR spectral data were in good agreement with the literature values.⁴⁷

***N*-(2-Furanylmethyl)-2-furanmethanamine (4w)**

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %) and Furfurylamine (97 mg, 1.0 mmol) was stirred at 130 °C for 16 h. The product **4w** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 70 mg, 79%). TLC; $R_f = 0.3$ (30% EtOAc in hexanes). Data for **4w**: ^1H NMR (400 MHz, CDCl_3) δ 7.40–7.31 (m, 2H), 6.34–6.27 (m, 2H), 6.22–6.13 (m, 2H), 3.78 (s, 4H), 1.89 (br s, 1H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 153.3, 141.9, 110.1, 107.2, 44.9 ppm; GC-MS for $\text{C}_{10}\text{H}_{11}\text{NO}_2$, $m/z = 177$ (M^+). ^1H and ^{13}C NMR spectral data were in good agreement with the literature values.⁴⁸

***N*-(3-Phenylpropyl)benzenepropanamine (4x)**

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %) and 3-phenyl-1-propanamine (135 mg, 1.0 mmol) was stirred at 130 °C for 16 h. The product **4x** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 53 mg, 42%). TLC; R_f = 0.3 (30% EtOAc in hexanes). Data for **4x**: ^1H NMR (400 MHz, CDCl_3) δ 7.34–7.14 (m, 10H), 2.65 (t, J = 7.4 Hz, 8H), 1.89 (brs, 1H), 1.84 (quintet, J = 7.4 Hz, 4H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 142.0, 128.3, 128.3, 125.8, 49.4, 33.6, 31.5 ppm; GC-MS for $\text{C}_{18}\text{H}_{23}\text{N}$, m/z = 253 (M^+). ^1H and ^{13}C NMR spectral data were in good agreement with the literature values.⁴¹

4-Methoxy-*N*-phenylbenzenemethanamine (5a)

A chlorobenzene (2.0 mL) solution of complex **1** (7 mg, 0.75 mol %), **L1** (8 mg, 10 mol %), aniline (47 mg, 0.5 mmol) and 4-methoxybenzylamine (96 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **5a** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 150:1 to 40:1; 76 mg, 71%). TLC; R_f = 0.4 (30% EtOAc in hexanes). Data for **5a**: ^1H NMR (400 MHz, CDCl_3) δ 7.29 (d, J = 8.6 Hz, 2H), 7.22–7.16 (m, 2H), 6.88 (d, J = 8.6 Hz, 2H), 6.77–6.72 (m, 1H), 6.70–6.65 (m, 2H), 4.26 (s, 2H), 3.80 (s, 3H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 158.9, 147.1, 130.6, 129.3, 129.1, 118.4, 114.0, 113.6, 55.3, 48.4 ppm; GC-MS for $\text{C}_{14}\text{H}_{15}\text{NO}$, m/z = 213 (M^+). ^1H and ^{13}C NMR spectral data were in good agreement with the literature values.^{49,50}

***N*-(4-Methoxyphenyl)phenylmethanamine (5b)**

A chlorobenzene (2.0 mL) solution of complex **1** (7 mg, 0.75 mol %), **L1** (8 mg, 10 mol %), 4-methoxyaniline (62 mg, 0.5 mmol) and benzylamine (75 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **5b** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 150:1 to 40:1; 61 mg, 57%). TLC; R_f = 0.3 (20% EtOAc in hexanes). Data for **5b**: ^1H NMR (400 MHz, CDCl_3) δ 7.46–7.29 (m, 5H), 6.87–6.81 (m, 2H), 6.69–6.63 (m, 2H), 4.33 (s, 2H), 3.79 (s, 3H), ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 152.1, 142.2, 139.5, 128.5, 127.5, 127.1, 114.8, 114.1, 55.7, 49.1 ppm; GC-MS for $\text{C}_{14}\text{H}_{15}\text{NO}$, m/z = 213 (M^+). ^1H and ^{13}C NMR spectral data were in good agreement with the literature values.^{51,52}

***N*-(4-Methoxyphenyl)[1,1'-biphenyl]-4-methanamine (5c)**

A chlorobenzene (2.0 mL) solution of complex **1** (7 mg, 0.75 mol %), **L1** (8 mg, 10 mol %), 4-methoxyaniline (62 mg, 0.5 mmol) and 4-phenylbenzylamine (128 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **5c** was isolated by a column chromatography on silica gel (*n*-hexane/ethyl acetate = 150:1 to 40:1; 101 mg, 70%). TLC; R_f = 0.4 (30% EtOAc in hexanes). Data for **5c**: ^1H NMR (400 MHz, CDCl_3) δ 7.61–7.55 (m, 4H), 7.47–7.42 (m, 4H), 7.35 (tt, J = 7.3, 1.3, Hz, 1H), 6.82–6.77 (m, 2H), 6.69–6.65 (m, 2H), 4.34 (s, 2H), 3.75 (s, 3H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 152.5, 141.7, 140.8, 140.2, 138.3, 128.7, 128.1, 127.3, 127.2, 127.0, 114.9, 114.6, 55.8, 49.2 ppm; GC-MS for $\text{C}_{20}\text{H}_{19}\text{NO}$, m/z = 289 (M^+). ^1H and ^{13}C NMR spectral data were in good agreement with the literature values.⁵³

4-Fluoro-*N*-(4-methoxyphenyl)benzenemethanamine (5d)

A chlorobenzene (2.0 mL) solution of complex **1** (7 mg, 0.75 mol %), **L1** (8 mg, 10 mol %), 4-methoxyaniline (62 mg, 0.5 mmol) and 4-fluorobenzylamine (88 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **5d** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 150:1 to 40:1; 47 mg, 41%). TLC; R_f = 0.3 (20% EtOAc in hexanes). Data for **5d**: ^1H NMR (400 MHz, CDCl_3) δ 7.38–7.30 (m, 2H), 7.07–6.99 (m, 2H), 6.83–6.76 (m, 2H), 6.66–6.59 (m, 2H), 4.26 (s, 2H), 4.09 (br s, 1H), 3.75 (s, 3H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 162.0 (d, J_{CF} = 245.1 Hz), 152.4, 141.7, 135.0 (d, J_{CF} = 3.1 Hz), 129.1 (d, J_{CF} = 8.0 Hz), 115.3 (d, J_{CF} = 21.4 Hz), 114.8, 114.4, 55.7, 48.6 ppm; GC-MS for $\text{C}_{14}\text{H}_{14}\text{FNO}$ m/z = 231 (M^+). ^1H and ^{13}C NMR spectral data were in good agreement with the literature values.^{54,55}

***N*-(4-Chlorophenyl)-4-methoxybenzenemethanamine (5e)**

A chlorobenzene (2.0 mL) solution of complex **1** (7 mg, 0.75 mol %), **L1** (8 mg, 10 mol %), 4-chloroaniline (64 mg, 0.5 mmol) and 4-methoxybenzylamine (96 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **5e** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 150:1 to 40:1; 73 mg, 59%). TLC; R_f = 0.5 (20% EtOAc in hexanes). Data for **5e**: ^1H NMR (400 MHz, CDCl_3) 7.30–7.25 (m, 2H), 7.14–7.09 (m, 2H), 6.92–6.87 (m, 2H), 6.59–6.53 (m, 2H), 4.23 (s, 2H), 4.15 (br s, 1H), 3.81 (s, 3H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 158.9, 146.5, 130.7, 129.0, 128.7, 122.1, 114.0, 114.0, 55.3, 47.9 ppm; GC-MS for $\text{C}_{14}\text{H}_{14}\text{ClNO}$, m/z = 247 (M^+). ^1H and ^{13}C NMR spectral data were in good agreement with the literature values.⁵⁶

3,4,5-Trimethoxy-*N*-(4-methoxyphenyl)benzenemethanamine (5f)

A chlorobenzene (2.0 mL) solution of complex **1** (7 mg, 0.75 mol %), **L1** (8 mg, 10 mol %), 4-methoxyaniline (62 mg, 0.5 mmol) and 3,4,5-trimethoxybenzylamine (138 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **5f** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 150:1 to 40:1; 138 mg, 91%). TLC; R_f = 0.5 (50% EtOAc in hexanes). Data for **5f**: ^1H NMR (400 MHz, CDCl_3) δ 6.81–6.76 (m, 2H), 6.65–6.60 (m, 4H), 4.21 (s, 2H), 3.84 (s, 9H), 3.74 (s, 3H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 153.3, 152.3, 142.1, 136.9, 135.3, 114.8, 114.3, 104.3, 60.8, 56.0, 55.7, 49.7 ppm; GC-MS for $\text{C}_{17}\text{H}_{21}\text{NO}_4$, m/z = 303 (M^+). ^1H and ^{13}C NMR spectral data were in good agreement with the literature values.^{57,58}

3,4,5-Trimethoxy-*N*-phenylbenzenemethanamine (5g)

A chlorobenzene (2.0 mL) solution of complex **1** (7 mg, 0.75 mol %), **L1** (8 mg, 10 mol %), aniline (47 mg, 0.5 mmol) and 3,4,5-trimethoxybenzylamine (138 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **5g** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 150:1 to 40:1; 97 mg, 71%). TLC; R_f = 0.6 (50% EtOAc in hexanes). Data for **5g**: ^1H NMR (400 MHz, CDCl_3) δ 7.23–7.17 (m, 2H), 6.75 (tt, J = 7.3, 1.1 Hz, 1H), 6.69–6.65 (m, 2H), 6.63 (s, 2H), 4.27 (s, 2H), 4.13 (br s, 1H), 3.86 (s, 3H), 3.85 (s, 6H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 153.3, 148.0, 136.8, 135.1, 129.1, 117.6, 112.8, 104.2, 60.7, 55.9, 48.7 ppm; GC-MS for $\text{C}_{16}\text{H}_{19}\text{NO}_3$, m/z = 273 (M^+). ^1H and ^{13}C NMR spectral data were in good agreement with the literature values.^{59,60}

3,4,5-Trimethoxy-*N*-(4-chlorophenyl)benzenemethanamine (5h)

A chlorobenzene (2.0 mL) solution of complex **1** (7 mg, 0.75 mol %), **L1** (8 mg, 10 mol %), 4-chloroaniline (64 mg, 0.5 mmol) and 3,4,5-trimethoxybenzylamine (138 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **5h** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 150:1 to 40:1; 111 mg, 72%). TLC; R_f = 0.6 (50% EtOAc in hexanes). Data for **5h**: ^1H NMR (400 MHz, CDCl_3) δ 7.12 (d, J = 9.0 Hz, 2H), 6.58 (s, 2H), 6.57 (d, J = 9.0 Hz, 2H), 4.23 (s, 2H), 3.84 (s, 3H), 3.84 (s, 6H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 153.4, 146.4, 137.0, 134.5, 129.0, 122.3, 114.0, 104.1, 60.8, 56.0, 48.8 ppm; GC-MS for $\text{C}_{16}\text{H}_{18}\text{ClNO}_3$, m/z = 307 (M^+). Anal. Calcd for $\text{C}_{16}\text{H}_{18}\text{ClNO}_3$: C, 62.44; H, 5.90. Found: C, 62.88; H, 6.05.

***N*-Hexyl-4-methoxybenzenamine (5i)**

A chlorobenzene (2.0 mL) solution of complex **1** (7 mg, 0.75 mol %), **L1** (8 mg, 10 mol %), 4-methoxyaniline (62 mg, 0.5 mmol) and 1-hexamine (71 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **5i** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 150:1 to 40:1; 65 mg, 63%). TLC; R_f = 0.4 (20% EtOAc in hexanes). Data for **5i**: ^1H NMR (400 MHz, CDCl_3) δ 6.82–6.77 (m, 2H), 6.63–6.58 (m, 2H), 3.75 (s, 3H), 3.39 (br s, 1H), 3.06 (t, J = 7.2 Hz, 2H), 1.61 (quintet, J = 7.4 Hz, 2H), 1.44–1.26 (m, 6H), 0.91 (t, J = 6.9 Hz, 3H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 152.1, 142.5, 114.8, 114.2, 55.8, 45.2, 31.6, 29.5, 26.8, 22.6, 14.0 ppm; GC-MS for $\text{C}_{13}\text{H}_{21}\text{NO}$, m/z = 207 (M^+). ^1H and ^{13}C NMR spectral data were in good agreement with the literature values.⁵⁸

***N*-(4-Methoxyphenyl)benzenepropanamine (5j)**

A chlorobenzene (2.0 mL) solution of complex **1** (7 mg, 0.75 mol %), **L1** (8 mg, 10 mol %), 4-methoxyaniline (62 mg, 0.5 mmol) and 3-phenyl-1-propanamine (95 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **5j** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 150:1 to 40:1; 54 mg, 45%). TLC; R_f = 0.9 (50% EtOAc in hexanes). Data for **5j**: ^1H NMR (400 MHz, CDCl_3) δ 7.34–7.29 (m, 2H), 7.25–7.18 (m, 3H), 6.80 (d, J = 8.9 Hz, 2H), 6.60 (d, J = 8.9 Hz, 2H), 3.76 (s, 3H), 3.13 (t, J = 7.1 Hz, 2H), 2.75 (t, J = 7.6 Hz, 2H), 1.96 (quintet, J = 7.4 Hz, 2H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 152.2, 142.2, 141.7, 128.4, 128.4, 125.9, 114.8, 114.3, 55.8, 44.6, 33.4, 31.0 ppm; GC-MS for $\text{C}_{16}\text{H}_{19}\text{NO}$, m/z = 241 (M^+). ^1H and ^{13}C NMR spectral data were in good agreement with the literature values.^{61,62}

***N*-(4-Methoxyphenyl)-2,3-dihydro-1H-inden-2-amine (5k)**

A chlorobenzene (2.0 mL) solution of complex **1** (7 mg, 0.75 mol %), **L1** (8 mg, 10 mol %), 3,4,5-trimethoxyaniline (62 mg, 0.5 mmol) and 2-aminoindan (93 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **5k** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 150:1 to 40:1; 88 mg, 74%). TLC; R_f = 0.5 (30% EtOAc in hexanes). Data for **5k**: ^1H NMR (400 MHz, CDCl_3) δ 7.29–7.17 (m, 4H), 6.86–6.80 (m, 2H), 6.67–6.62 (m, 2H), 4.33 (tt, J = 6.8, 4.4 Hz, 1H), 3.79 (s, 3H), 3.37 (dd, J = 16.0, 6.8 Hz, 2H), 2.90 (dd, J = 16.0, 4.4 Hz, 2H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 152.2, 141.4, 141.4, 126.5, 124.9, 114.9, 114.9, 55.7, 54.9, 40.1 ppm; GC-MS for $\text{C}_{16}\text{H}_{17}\text{NO}$, m/z = 239 (M^+); HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{16}\text{H}_{17}\text{NOH}$ 240.1383; Found 240.1377.

4-(2-(3,4,5-Trimethoxyphenylamino)ethyl)phenol (5l)

A chlorobenzene (2.0 mL) solution of complex **1** (7 mg, 0.75 mol %), **L1** (8 mg, 10 mol %), 3,4,5-trimethoxyaniline (91 mg, 0.5 mmol) and 2-(4-hydroxyphenyl)ethanamine (96 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **5l** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 150:1 to 40:1; 77 mg, 51%). TLC; R_f = 0.4 (50% EtOAc in hexanes). Data for **5l**: ^1H NMR (400 MHz, CDCl_3) δ 7.09–7.05 (m, 2H), 6.81–6.77 (m, 2H), 5.90 (s, 2H), 3.81 (s, 6H), 3.77 (s, 3H), 3.33 (t, J = 7.1 Hz, 2H), 2.86 (t, J = 7.1 Hz, 2H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 154.4, 153.9, 144.1, 130.7, 130.5, 129.8, 115.5, 91.1, 61.1, 55.9, 46.2, 34.4 ppm; GC-MS for $\text{C}_{17}\text{H}_{21}\text{NO}_4$, m/z = 303 (M^+); HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{17}\text{H}_{21}\text{NO}_4$ 304.1543; Found 304.1516.

N-(3,4,5-Trimethoxybenzyl)-3,4-dihydro-2H-benzo[b][1,4]dioxepin-7-amine (5m)

A chlorobenzene (2.0 mL) solution of complex **1** (7 mg, 0.75 mol %), **L1** (8 mg, 10 mol %), 3,4-dihydro-2H-1,5-benzodioxepin-7-amine (83 mg, 0.5 mmol) and 3,4,5-trimethoxybenzylamine (138 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **5m** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 150:1 to 40:1; 129 mg, 75%). TLC; R_f = 0.4 (50% EtOAc in hexanes). Data for **5m**: ^1H NMR (400 MHz, CDCl_3) δ 6.84 (d, J = 8.6 Hz, 1H), 6.59 (s, 2H), 6.38–6.34 (m, 1H), 6.31–6.26 (m, 1H), 4.19 (s, 2H), 4.15 (t, J = 5.4 Hz, 2H), 4.09 (t, J = 5.5 Hz, 2H), 3.84 (s, 6H), 3.83 (s, 3H), 2.14 (quintet, J = 5.5 Hz, 2H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 153.3, 152.1, 143.9, 143.6, 137.0, 134.4, 122.2, 108.7, 106.5, 104.5, 70.9, 70.8, 60.8, 56.1, 49.8, 32.4 ppm; GC-MS for $\text{C}_{19}\text{H}_{23}\text{NO}_5$, m/z = 345 (M^+); HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{19}\text{H}_{23}\text{FNO}_5\text{H}$ 346.1649; Found 346.1618.

N-(3,5-Dimethoxybenzyl)-4-methoxybenzenamine (5n)

A chlorobenzene (2.0 mL) solution of complex **1** (7 mg, 0.75 mol %), **L1** (8 mg, 10 mol %), 4-methoxyaniline (62 mg, 0.5 mmol) and 3,5-dimethoxybenzylamine (117 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **5n** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 150:1 to 40:1; 115 mg, 84%). TLC; R_f = 0.7 (50% EtOAc in hexanes). Data for **5n**: δ ^1H NMR (400 MHz, CDCl_3) 6.82–6.77 (m, 2H), 6.64–6.59 (m, 2H), 6.57 (d, J = 2.3 Hz, 2H), 6.40 (t, J = 2.3 Hz, 1H), 4.23 (s, 2H), 3.79 (s, 6H), 3.76 (s, 3H), ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 160.9, 152.0, 142.3, 142.2, 114.7, 114.0, 105.2, 98.9, 55.6, 55.2, 49.2 ppm; GC-MS for $\text{C}_{16}\text{H}_{19}\text{NO}_3$, m/z = 273 (M^+). ^1H and ^{13}C NMR spectral data were in good agreement with the literature values.⁶³

4-Chloro-N-(3,5-dimethoxybenzyl)benzenamine (5o)

A chlorobenzene (2.0 mL) solution of complex **1** (7 mg, 0.75 mol %), **L1** (8 mg, 10 mol %), 4-chloroaniline (64 mg, 0.5 mmol) and 3,5-dimethoxybenzylamine (117 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **5o** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 150:1 to 40:1; 66 mg, 48%). TLC; R_f = 0.6 (30% EtOAc in hexanes). Data for **5o**: ^1H NMR (400 MHz, CDCl_3) δ 7.13–7.08 (m, 2H), 6.58–6.53 (m, 2H), 6.52–6.49 (m, 2H), 6.38 (t, J = 2.2 Hz, 1H), 4.24 (s, 2H), 3.78 (s, 6H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 161.1, 146.3, 141.3, 129.0, 122.3, 114.1, 105.2, 99.1, 55.3, 48.6

ppm; GC-MS for $C_{15}H_{16}ClNO_2$, $m/z = 277$ (M^+); HRMS (ESI-TOF) m/z : $[M+H]^+$ Calcd for $C_{15}H_{16}NO_2ClH$ 278.0942; Found 278.0928.

***N*-(3,5-Dimethoxybenzyl)-4-(trifluoromethyl)benzenamine (5p)**

A chlorobenzene (2.0 mL) solution of complex **1** (7 mg, 0.75 mol %), **L1** (8 mg, 10 mol %), 4-trifluoromethylaniline (81 mg, 0.5 mmol) and 3,5-dimethoxybenzylamine (117 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **5p** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 150:1 to 40:1; 58 mg, 37%). TLC; $R_f = 0.4$ (30% EtOAc in hexanes). Data for **5p**: 1H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, $J = 8.6$ Hz, 2H), 6.63 (d, $J = 8.6$ Hz, 2H), 6.51 (d, $J = 2.3$ Hz, 2H), 6.39 (t, $J = 2.3$ Hz, 1H), 4.55 (br s, 1H), 4.30 (s, 2H), 3.78 (s, 6H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 161.1, 150.3, 140.9, 126.6 (q, $J_{CF} = 3.8$ Hz), 124.9 (q, $J_{CF} = 270.6$ Hz), 119.2 (q, $J_{CF} = 32.6$ Hz), 112.1, 105.2, 99.1, 55.3, 48.0 ppm; GC-MS for $C_{16}H_{16}F_3NO_2$, $m/z = 311$ (M^+); HRMS (ESI-TOF) m/z : $[M+H]^+$ Calcd for $C_{16}H_{16}F_3NO_2H$ 312.1206; Found 312.1207.

9-Ethyl-*N*-hexyl-9H-carbazol-3-amine (5q)

A chlorobenzene (2.0 mL) solution of complex **1** (7 mg, 0.75 mol %), **L1** (8 mg, 10 mol %), 3-amino-9-ethylcarbazole (105 mg, 0.5 mmol) and 1-hexamine (71 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **5q** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 150:1 to 40:1; 103 mg, 70%). TLC; $R_f = 0.4$ (50% EtOAc in hexanes). Data for **5q**: 1H NMR (400 MHz, $CDCl_3$) δ 8.09–8.04 (m, 1H), 7.48–7.42 (m, 1H), 7.40–7.34 (m, 2H), 7.26 (d, $J = 7.3$ Hz, 1H), 7.19 (dd, $J = 7.3, 1.2$ Hz, 1H), 6.91 (dd, $J = 8.6, 2.3$ Hz, 1H), 4.32 (q, $J = 7.2$ Hz, 2H), 3.40 (br s, 1H), 3.25 (t, $J = 7.2$ Hz, 2H), 1.72 (quintet, $J = 7.4$ Hz, 2H), 1.55–1.45 (m, 2H), 1.42 (t, $J = 7.2$ Hz, 3H), 1.41–1.33 (m, 4H), 1.12–0.92 (m, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 141.9, 140.2, 133.9, 125.2, 123.6, 122.6, 120.3, 117.8, 114.6, 109.0, 108.3, 103.3, 45.7, 37.4, 31.7, 29.7, 27.0, 22.6, 14.0, 13.8 ppm; GC-MS for $C_{20}H_{26}N_2$, $m/z = 294$ (M^+); HRMS (ESI-TOF) m/z : $[M+H]^+$ Calcd for $C_{20}H_{26}N_2H$ 295.2169; Found 295.2167.

(*R*)-3-Ethyl-3-(4-(3,4,5-trimethoxybenzylamino)phenyl)piperidine-2,6-dione (5r)

A chlorobenzene (2.0 mL) solution of complex **1** (7 mg, 0.75 mol %), **L1** (8 mg, 10 mol %), (*R*)-(+)-aminogluthethimide (116 mg, 0.5 mmol) and 3,4,5-trimethoxybenzylamine (138 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **5r** was isolated by a column chromatography on silica gel (*n*-hexane/ethyl acetate = 100:1 to 1:1; 82 mg, 40%), $n_D^{20} = 1.482$ ($c = 0.2$ in CH_2Cl_2); TLC; $R_f = 0.2$ (50% EtOAc in hexanes). Data for **5r**: δ 7.98 (br s, 1H), 7.07 (d, $J = 8.7$ Hz, 2H), 6.64 (d, $J = 8.7$ Hz, 2H), 6.59 (s, 2H), 4.24 (s, 2H), 3.83 (s, 9H), 2.62–2.52 (m, 1H), 2.44 (dd, $J = 13.2, 4.9$ Hz, 1H), 2.31 (ddd, $J = 14.2, 4.8, 2.7$ Hz, 1H), 2.16 (dd, $J = 13.8, 4.8$ Hz, 1H), 1.99 (sext, $J = 7.4$ Hz, 1H), 1.87 (sextet, $J = 7.4$ Hz, 1H), 0.85 (t, $J = 7.4$ Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 175.5, 172.5, 153.4, 147.0, 137.1, 134.5, 127.1, 113.4, 113.4, 104.4, 60.8, 56.1, 50.2, 48.9, 32.9, 29.3, 26.9, 9.0 ppm; GC-MS for $C_{23}H_{28}N_2O_5$, $m/z = 412$ (M^+); HRMS (IT-TOF/ESI) Calcd for $C_{23}H_{28}N_2O_5-H$ ($[M-H]^-$): 411.1925, Found: 411.1908.

3-(3-Phenylpropylamino)piperidine-2,6-dione (5s)

A chlorobenzene (2.0 mL) solution of complex **1** (7 mg, 0.75 mol %), **L1** (8 mg, 10 mol %), L-glutamine (73 mg, 0.5 mmol) and 3-phenyl-1-propanamine (95 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **5s** was isolated by a column chromatography on silica gel (*n*-hexane/ethyl acetate = 50:1 to 1:1; 92 mg, 75%). TLC; R_f = 0.2 (50% EtOAc in hexanes). Data for **5s**: δ 7.30–7.23 (m, 2H), 7.22–7.12 (m, 3H), 6.73 (br s, 1H), 4.08 (dd, J = 9.0, 4.8 Hz, 1H), 3.28 (dd, J = 8.9, 4.8 Hz, 1H), 2.63 (t, J = 7.5 Hz, 2H), 2.50–2.37 (m, 1H), 2.37–2.19 (m, 2H), 2.16–2.05 (m, 1H), 1.84 (quintet, J = 7.4 Hz, 2H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 179.5, 172.1, 141.4, 128.4, 128.3, 126.0, 57.1, 39.3, 33.2, 30.8, 29.4, 25.7 ppm; GC-MS for $\text{C}_{14}\text{H}_{18}\text{N}_2\text{O}_2$, m/z = 246 (M^+); HRMS (ESI-TOF) m/z : [$\text{M}+\text{H}$] $^+$ Calcd for $\text{C}_{14}\text{H}_{18}\text{N}_2\text{O}_2\text{H}$ 247.1441; Found 247.1408.

3-(4-Methoxybenzylamino)piperidine-2,6-dione (5t)

A chlorobenzene (2.0 mL) solution of complex **1** (7 mg, 0.75 mol %), **L1** (8 mg, 10 mol %), L-glutamine (73 mg, 0.5 mmol) and 4-methoxybenzylamine (96 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **5t** was isolated by a column chromatography on silica gel (*n*-hexane/ethyl acetate = 50:1 to 1:1; 87 mg, 70%). TLC; R_f = 0.2 (50% EtOAc in hexanes). Data for **5t** δ 7.18 (d, J = 8.5 Hz, 2H), 6.92 (br s, 1H), 6.83 (d, J = 8.5 Hz, 2H), 4.40–4.29 (m, 2H), 4.13 (dd, J = 9.0, 4.7 Hz, 1H), 3.77 (s, 3H), 2.53–2.41 (m, 1H), 2.34–2.20 (m, 2H), 2.20–2.09 (m, 1H), 1.87 (br s, 1H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 179.5, 172.2, 158.8, 130.1, 128.9, 113.8, 57.0, 55.1, 42.7, 29.2, 25.5 ppm; GC-MS for $\text{C}_{13}\text{H}_{16}\text{N}_2\text{O}_3$, m/z = 248 (M^+); HRMS (ESI-TOF) m/z : [$\text{M}+\text{H}$] $^+$ Calcd for $\text{C}_{13}\text{H}_{16}\text{N}_2\text{O}_3\text{H}$ 249.1334; Found 249.1202.

Supplementary Material

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References

1. Recent reviews on the catalytic oxidative C–N activation reactions: Ouyang K, Hao W, Zhang WX, Xi Z. Transition-Metal-Catalyzed Cleavage of C–N Single Bonds. *Chem Rev.* 2015; 115:12045–12090. [PubMed: 26423200] Wang Q, Su Y, Li L, Huang H. Transition-metal catalysed C–N bond activation. *Chem Soc Rev.* 2016; 45:1257–1272. [PubMed: 26764537]
2. Selected examples of catalytic C–N bond cleavage reactions: Gandelman M, Milstein D. Homogeneously catalyzed, chelate assisted hydrogenolysis of an amine C–N bond. *Chem Commun.* 2000:1603–1604. Hosokawa T, Kamiike T, Murahashi S-I, Shimada M, Sugafuji T. The Heck reaction in the presence of molecular oxygen. *Tetrahedron Lett.* 2002; 43:9323–9325. Caddick S, Cloke FGN, Hitchcock PB, de Lewis KAK. Unusual Reactivity of a Nickel N-Heterocyclic Carbene Complex: *tert*-Butyl Group Cleavage and Silicone Grease Activation. *Angew Chem, Int Ed.* 2004; 43:5824–5827. Takano K, Inagaki A, Akita M. Chelation-assisted Facile C–N Bond Oxidative Addition of Spironaphthoxazines by $\text{Ru}(\eta^4\text{-cycloocta-1,5-diene})(\eta^6\text{-naphthalene})$. *Chem Lett.* 2006; 35:434–435. Burling S, Mahon MF, Powell RE, Whittlesey MK, Williams MJ. Ruthenium Induced C–N Bond Activation of an N-Heterocyclic Carbene: Isolation of C- and N-Bound

- Tautomers. *J Am Chem Soc.* 2006; 128:13702–13703. [PubMed: 17044694] Ueno S, Chatani N, Kakiuchi F. Ruthenium-Catalyzed Carbon-Carbon Bond Formation via the Cleavage of an Unreactive Aryl Carbon-Nitrogen Bond in Aniline Derivatives with Organoboronates. *J Am Chem Soc.* 2007; 129:6098–6099. [PubMed: 17444647] Zou B, Jiang H-F, Wang Z-Y. Palladium-Catalyzed C–N Bond Activation: The Synthesis of β -Amino Acid Derivatives from Triethylamine and Acrylates. *Eur J Org Chem.* 2007:4600–4604. Kruger K, Tillack A, Beller M. Recent Innovative Strategies for the Synthesis of Amines: From C–N Bond Formation to C–N Bond Activation. *Chem Sus Chem.* 2009; 2:715–717. Kuninobu Y, Nishi M, Takai K. Iron-catalyzed synthesis of glycine derivatives *via* carbon–nitrogen bond cleavage using diazoacetate. *Chem Commun.* 2010:8860–8862. Shen H, Wang Y, Xie Z. Ti-amide Catalyzed Synthesis of Cyclic Guanidines from Di-/Triamines and Carbodiimides. *Org Lett.* 2011; 13:4562–4565. [PubMed: 21815662] Jin Y-H, Fang F, Zhang X, Liu Q-Z, Wang H-B, Tian S-K. Four-Component Reaction of N-Sulfonylimines, (Cyanomethylene)triphenylphosphorane, Nitromethane, and Formaldehyde for the Synthesis of 3-Substituted 2-Methylene-4-nitrobutanenitriles. *J Org Chem.* 2011; 76:4163–4167. [PubMed: 21462971] Fukumoto K, Oya T, Itazaki M, Nakazawa H. N–CN Bond Cleavage of Cyanamides by a Transition-Metal Complex. *J Am Chem Soc.* 2009; 131:38–39. [PubMed: 19128169] Anbarasan P, Neumann H, Beller M. A General Rhodium-Catalyzed Cyanation of Aryl and Alkenyl Boronic Acids. *Angew Chem, Int Ed.* 2011; 50:519–522.
3. Akiyama F, Miyazaki H, Kaneda K, Teranishi S, Fujiwara Y, Abe M, Taniguchi H. Arylation and Alkylation of Olefins by Arylamines or Hydrazines via Carbon-Nitrogen Bond Cleavage in the Presence of Palladium(II) Salts. *J Org Chem.* 1980; 45:2359–2361.
 4. Koreeda T, Kochi T, Kakiuchi F. Cleavage of C–N Bonds in Aniline Derivatives on a Ruthenium Center and Its Relevance to Catalytic C–C Bond Formation. *J Am Chem Soc.* 2009; 131:7238–7239. [PubMed: 19432447]
 5. (a) Hie L, Fine NNF, Shah TK, Baker EL, Hong X, Yang YF, Liu P, Houk KN, Garg NK. Conversion of amides to esters by the nickel-catalysed activation of amide C–N bonds. *Nature.* 2015; 524:79–83. [PubMed: 26200342] (b) Meng G, Shi S, Szostak M. Cross-Coupling of Amides by N–C Bond Activation. *Synlett.* 2016; 27:2530–2540. (c) Liu C, Szostak M. Twisted Amides: From Obscurity to Broadly Useful Transition-Metal-Catalyzed Reactions by N–C Amide Bond Activation. *Chem Eur J.* 2017; 23:7157–7173. [PubMed: 27813178]
 6. (a) Weston MH, Parvez M, Back TG. *J Org Chem.* 2010; 75:5402–5405. [PubMed: 20614920] (b) Wang M, Zhang X, Zhuang Y-X, Xu Y-H, Loh T-P. Pd-Catalyzed Intramolecular C–N Bond Cleavage, 1,4-Migration, sp^3 C–H Activation, and Heck Reaction: Four Controllable Diverse Pathways Depending on the Judicious Choice of the Base and Ligand. *J Am Chem Soc.* 2015; 137:1341–1347. [PubMed: 25545361] (c) Meng G, Szostak M. General Olefin Synthesis by the Palladium-Catalyzed Heck Reaction of Amides: Sterically Controlled Chemoselective Activation. *Angew Chem, Int Ed.* 2015; 54:14518–14522. (d) Shi S, Meng G, Szostak M. Synthesis of Biaryls through Nickel-Catalyzed Suzuki–Miyaura Coupling of Amides by Carbon–Nitrogen Bond Cleavage. *Angew Chem, Int Ed.* 2016; 55:6959–6963.
 7. (a) Mukherjee S, List B. Chiral Counteranions in Asymmetric Transition-Metal Catalysis: Highly Enantioselective Pd/Brønsted Acid-Catalyzed Direct γ -Allylation of Aldehydes. *J Am Chem Soc.* 2007; 129:11336–11337. [PubMed: 17715928] (b) Wu X-S, Chen Y, Li M-B, Zhou M-G, Tian S-K. Direct Substitution of Primary Allylic Amines with Sulfinate Salts. *J Am Chem Soc.* 2012; 134:14694–14697. [PubMed: 22928707] (c) Li MB, Wang Y, Tian S-K. Regioselective and Stereospecific Cross-Coupling of Primary Allylic Amines with Boronic Acids and Boronates through Palladium-Catalyzed C–N Bond Cleavage. *Angew Chem, Int Ed.* 2012; 51:2968–2971. (d) Ma X-T, Wang Y, Dai R-H, Liu C-R, Tian S-K. Catalytic Allylation of Stabilized Phosphonium Ylides with Primary Allylic Amines. *J Org Chem.* 2013; 78:11071–11075. [PubMed: 24093555]
 8. Liu CR, Li MB, Cheng DJ, Yang CF, Tian SK. Catalyst-Free Alkylation of Sulfinic Acids with Sulfonamides via sp^3 C–N Bond Cleavage at Room Temperature. *Org Lett.* 2009; 11:2543–2545. [PubMed: 19449883]
 9. Li BJ, Wang HY, Zhu QL, Shi ZJ. Rhodium/Copper-Catalyzed Annulation of Benzimides with Internal Alkynes: Indenone Synthesis through Sequential C–H and C–N Cleavage. *Angew Chem, Int Ed.* 2012; 51:3948–3952.

10. Balaraman E, Gnanaprakasam G, Shimon LJW, Milstein D. Direct Hydrogenation of Amides to Alcohols and Amines under Mild Conditions. *J Am Chem Soc.* 2010; 132:16756–16758. [PubMed: 21049928]
11. (a) Lei Y, Wroblewski AD, Golden JE, Powell DR, Aube J. Facile C–N Cleavage in a Series of Bridged Lactams. *J Am Chem Soc.* 2005; 127:4552–4553. [PubMed: 15796502] (b) Kajita Y, Matsubara S, Kurahashi T. Nickel-Catalyzed Decarbonylative Addition of Phthalimides to Alkynes. *J Am Chem Soc.* 2008; 130:6058–6059. [PubMed: 18412348] (c) Li C, Zhang W-T, Wang X-S. CuI-Catalyzed C–N Bond Formation and Cleavage for the Synthesis of Benzimidazo[1,2- α]quinazoline Derivatives. *J Org Chem.* 2014; 79:5847–5851. [PubMed: 24885515] (d) Yang X-F, Hu X-H, Loh T-P. Expedient Synthesis of Pyrroloquinolinones by Rh-Catalyzed Annulation of N-Carbamoyl Indolines with Alkynes through a Directed C–H Functionalization/C–N Cleavage Sequence. *Org Lett.* 2015; 17:1481–1484. [PubMed: 25754346] (e) Shi S, Szostak M. Nickel-Catalyzed Diaryl Ketone Synthesis by N–C Cleavage: Direct Negishi Cross-Coupling of Primary Amides by Site-Selective N, N-DiBoc Activation. *Org Lett.* 2016; 18:5872–5875. [PubMed: 27934487] (f) Hu F, Lalancette R, Szostak M. Structural Characterization of N-Alkylated Twisted Amides: Consequences for Amide Bond Resonance and N–C Cleavage. *Angew Chem, Int Ed.* 2016; 55:5062–5066.
12. Recent reviews: Hamid MHSA, Slatford PA, Williams MJ. Borrowing Hydrogen in the Activation of Alcohols. *Adv Synth Catal.* 2007; 349:1555–1575. Dobereiner GE, Crabtree RH. Dehydrogenation as a Substrate-Activating Strategy in Homogeneous Transition-Metal Catalysis. *Chem Rev.* 2010; 110:681–703. [PubMed: 19938813] Guillena G, Ramon DJ, Yus M. Hydrogen Autotransfer in the N-Alkylation of Amines and Related Compounds using Alcohols and Amines as Electrophiles. *Chem Rev.* 2010; 110:1611–1641. [PubMed: 19928825] Yang Q, Wanga Q, Yu Z. Substitution of alcohols by N-nucleophiles via transition metal-catalyzed dehydrogenation. *Chem Soc Rev.* 2015; 44:2305–2329. [PubMed: 25661436]
13. (a) Yan T, Feringa BL, Barta K. Iron catalysed direct alkylation of amines with alcohols. *Nat Commun.* 2014; 5:5602–5609. [PubMed: 25424885] (b) Rosler S, Ertl M, Irrgang T, Kempe R. Cobalt Catalyzed Alkylation of Aromatic Amines by Alcohols. *Angew Chem, Int Ed.* 2015; 54:15046–15050. (c) Elangovan S, Neumann J, Sortais J-B, Junge K, Darcel C, Beller M. Efficient and selective N-alkylation of amines with alcohols catalysed by manganese pincer complexes. *Nat Commun.* 2016; 7:12641–12649. [PubMed: 27708259] (d) Mukherjee A, Nerush A, Leitus G, Shimon LJW, David YB, Jalapa NAE, Milstein D. Manganese-Catalyzed Environmentally Benign Dehydrogenative Coupling of Alcohols and Amines to Form Aldimines and H₂: A Catalytic and Mechanistic Study. *J Am Chem Soc.* 2016; 138:4298–4301. [PubMed: 26924231] (e) Vellakkaran M, Singh K, Banerjee D. An Efficient and Selective Nickel-Catalyzed Direct N-Alkylation of Anilines with Alcohols. *ACS Catal.* 2017; 7:8152–8158.
14. Recent reviews: Baxter EW, Reitz AB. Reductive Aminations of Carbonyl Compounds with Borohydride and Borane Reducing Agents. *Org React.* 2002; 59:1–715. Gomez S, Peters JA, Maschmeyer T. The Reductive Amination of Aldehydes and Ketones and the Hydrogenation of Nitriles: Mechanistic Aspects and Selectivity Control. *Adv Synth Catal.* 2002; 344:1037–1057. Tripathi RP, Verma SS, Pandey J, Tiwari VK. Recent Development on Catalytic Reductive Amination and Applications. *Curr Org Chem.* 2008; 12:1093–1115.
15. Hollmann D, Bahn S, Tillack A, Beller M. N-Dealkylation of aliphatic amines and selective synthesis of monoalkylated aryl amines. *Chem Commun.* 2008:3199–3201.
16. Zhao X, Liu D, Guo H, Liu Y, Zhang W. C–N Bond Cleavage of Allylic Amines via Hydrogen Bond Activation with Alcohol Solvents in Pd-Catalyzed Allylic Alkylation of Carbonyl Compounds. *J Am Chem Soc.* 2011; 133:19354–19357. [PubMed: 22050268]
17. (a) Kim J, Lee DH, Kalutharage N, Yi CS. Selective Catalytic Synthesis of Unsymmetrical Ethers from the Dehydrative Etherification of Two Different Alcohols. *ACS Catal.* 2014; 4:3881–3885. (b) Kalutharage N, Yi CS. Chemoselective Formation of Unsymmetrically Substituted Ethers from Catalytic Reductive Coupling of Aldehydes and Ketones with Alcohols in Aqueous Solution. *Org Lett.* 2015; 17:1778–1781. [PubMed: 25803313]
18. Kalutharage N, Yi CS. Scope and Mechanistic Analysis for Chemoselective Hydrogenolysis of Carbonyl Compounds Catalyzed by a Cationic Ruthenium Hydride Complex with a Tunable Phenol Ligand. *J Am Chem Soc.* 2015; 137:11105–11114. [PubMed: 26235841]

19. (a) Singleton DA, Thomas AA. High-Precision Simultaneous Determination of Multiple Small Kinetic Isotope Effects at Natural Abundance. *J Am Chem Soc.* 1995; 117:9357–9358. (b) Frantz DE, Singleton DA, Snyder JP. ^{13}C Kinetic Isotope Effects for the Addition of Lithium Dibutylcuprate to Cyclohexenone. Reductive Elimination Is Rate-Determining. *J Am Chem Soc.* 1997; 119:3383–3384. (c) Nowlan DT, Gregg TM, Davies HML, Singleton DA. Isotope Effects and the Nature of Selectivity in Rhodium-Catalyzed Cyclopropanations. *J Am Chem Soc.* 2003; 125:15902–15911. [PubMed: 14677982]
20. (a) Brown RS, Ulan JG. Hydrolysis of Imidazole-Containing Amide Acetals. *J Am Chem Soc.* 1983; 105:2382–2388. (b) Nuiry II, Hermes JD, Weiss PM, Chen CY, Cook PF. Kinetic Mechanism and Location of Rate-Determining Steps for Aspartase from *Hafnia alvei*. *Biochemistry.* 1984; 23:5168–5175. [PubMed: 6509019] (c) Manoharan TS, Brown RS. 1-(1-Ethoxyethyl): An Effective Protecting Group for Imidazole Nitrogen. *J Org Chem.* 1988; 53:1107–1110. (d) Reyes MB, Carpenter BK. Mechanism of Thermal Deazetization of 2,3-Diazabicyclo[2.2.1]hept-2-ene and Its Reaction Dynamics in Supercritical Fluids. *J Am Chem Soc.* 2000; 122:10163–10176. (e) Fast W, Wang Z, Benkovic SJ. Familial Mutations and Zinc Stoichiometry Determine the Rate-Limiting Step of Nitrocefin Hydrolysis by Metallo- α -lactamase from *Bacteroides fragilis*. *Biochemistry.* 2001; 40:1640–1650. [PubMed: 11327823]
21. Eubanks JRI, Sims LB, Fry A. Carbon Isotope Effect Studies of the Mechanism of the Hofmann Elimination Reaction of Para-Substituted (2-Phenylethyl-1- ^{14}C)- and (2-Phenylethyl-2- ^{14}C)trimethylammonium Bromides. *J Am Chem Soc.* 1991; 113:8821–8829.
22. Marlier JF, Robins LI, Tucker KA, Rawlings J, Anderson MA, Cleland WW. A Kinetic and Isotope Effect Investigation of the Urease-Catalyzed Hydrolysis of Hydroxyurea. *Biochemistry.* 2010; 49:8213–8219. [PubMed: 20695482]
23. In an effort to demonstrate the reversibility of the imine formation, we performed the reaction of $\text{PhN}=\text{CHPh}$ (1.0 mmol) with cyclohexylamine (1.4 mmol) in the presence of 1/L1 at 130 °C. The reaction produced a complex mixture of aniline and the crossover products, $\text{PhN}=\text{CC}_5\text{H}_{10}$, $(\text{PhCH}_2)_2\text{NH}$, PhCH_2NHCy and $\text{PhCH}_2\text{N}=\text{CC}_5\text{H}_{10}$.
24. (a) Wu JC, Song RJ, Wang ZQ, Huang XC, Xie YX, Li JH. Copper-Catalyzed C-H Oxidation/Cross-Coupling of α -Amino Carbonyl Compounds. *Angew Chem, Int Ed.* 2012; 51:3453–3457. (b) Tian J-S, Loh T-P. Copper-Catalyzed Rearrangement of Tertiary Amines through Oxidation of Aliphatic C-H Bonds in Air or Oxygen: Direct Synthesis of α -Amino Acetals. *Angew Chem, Int Ed.* 2010; 49:8417–8420. (c) Guo S, Qian B, Xie Y, Xia C, Huang H. Copper-Catalyzed Oxidative Amination of Benzoxazoles via C-H and C-N Bond Activation: A New Strategy for Using Tertiary Amines as Nitrogen Group Sources. *Org Lett.* 2011; 13:522–525. [PubMed: 21182335] (d) Wan J-P, Zhou Y, Cao S. Domino Reactions Involving the Branched C–N and C–C Cleavage of Enaminones Toward Pyridines Synthesis. *J Org Chem.* 2014; 79:9872–9877. [PubMed: 25232686]
25. Selected reviews: Theophanides T, Harvey PD. Structural and spectroscopic properties of metal-urea complexes. *Coord Chem Rev.* 1987; 76:237–264. Borovik AS. Bioinspired Hydrogen Bond Motifs in Ligand Design: The Role of Noncovalent Interactions in Metal Ion Mediated Activation of Dioxygen. *Acc Chem Res.* 2005; 38:54–61. [PubMed: 15654737] Shao J-Y, Gong Z-L, Zhong Y-W. Bridged cyclometalated diruthenium complexes for fundamental electron transfer studies and multi-stage redox switching. *Dalton Trans.* 2018; 47:23–29. [PubMed: 29230470]
26. In a NMR tube, the heating of 1 (0.01 mmol) with L1 (0.04 mmol) in toluene- d_8 at 80 °C for 6 h led to the formation of a new Ru complex, which exhibited two signals in the $^{31}\text{P}\{^1\text{H}\}$ NMR (δ 56.1 and 56.6 ppm) but did not show any Ru-H peaks in the ^1H NMR.
27. Jadhav AR, Bandal HA, Kim H. Synthesis of Substituted Amines: Catalytic Reductive Amination of Carbonyl Compounds using Lewis Acid Zn–Co-Double Metal Cyanide/Polymethylhydrosiloxane. *Chem Eng J.* 2016; 295:376–383.
28. Bregeot NF, Raushel J, Sandrock DL, Dreher SD, Molander GA. Rapid and Efficient Access to Secondary Arylmethylamines. *Chem Eur J.* 2012; 18:9564–9570. [PubMed: 22767518]
29. Ehmke V, Winkler E, Banner DW, Haap W, Schweizer WB, Rottmann M, Kaiser M, Freymond C, Schirmeister T, Diederich F. Optimization of Triazine Nitriles as Rhodesain Inhibitors: Structure–Activity Relationships, Bioisosteric Imidazopyridine Nitriles, and X-ray Crystal Structure Analysis with Human Cathepsin. *Chem Med Chem.* 2013; 8:967–975. [PubMed: 23658062]

30. Huang PQ, Geng H. Simple, Versatile, and Chemoselective Reduction of Secondary Amides and Lactams to Amines with the $\text{TiF}_2\text{O}-\text{NaBH}_4$ or $\text{Cp}_2\text{ZrHCl}-\text{NaBH}_4$ System. *Org Chem Front.* 2015; 2:150–158.
31. (a) Majumdar B, Mandani S, Bhattacharya T, Sarma D, Sarma TK. Probing Carbocatalytic Activity of Carbon Nanodots for the Synthesis of Biologically Active Dihydro/Spiro/Glyco Quinazolinones and Aza-Michael Adducts. *J Org Chem.* 2017; 82:2097–2106. [PubMed: 28121145] (b) Kalita P, Pegu CD, Dutta P, Baruah PK. Room Temperature Solvent Free Aza-Michael Reactions over Nano-cage Mesoporous Materials. *J Mol Cat A.* 2014; 394:145–150.
32. Smith CJ, Smith CD, Nikbin N, Ley SV, Baxendale IR. Flow Synthesis of Organic Azides and the Multistep Synthesis of Imines and Amines using a New Monolithic Triphenylphosphine Reagent. *Org Biomol Chem.* 2011; 9:1927–1937. [PubMed: 21283873]
33. Martínez PH, Hultsch KC, Gil A, Branchadell V. Base-Catalyzed Anti-Markovnikov Hydroamination of Vinylarenes – Scope, Limitations and Computational Studies. *Eur J Org Chem.* 2007; 20:3311–3325.
34. Ehmke V, Heindl C, Rottmann M, Freymond C, Schweizer WB, Brun R, Stich A, Schirmeister T, Diederich F. Potent and Selective Inhibition of Cysteine Proteases from *Plasmodium falciparum* and *Trypanosoma brucei*. *Chem Med Chem.* 2011; 6:273–278. [PubMed: 21275051]
35. Murali R, Rao HSP, Scheeren HW. Intra-Molecular Diels–Alder Reactions of Citraconamic Acids from Furfurylamines and Citraconic Anhydride: Effects of Substitution in the Furan Ring on Regioselectivity. *Tetrahedron.* 2001; 57:3165–3174.
36. Su C, Tandiana R, Balapanuru J, Tang W, Pareek K, Nai CT, Hayashi T, Loh KP. Tandem Catalysis of Amines using Porous Graphene Oxide. *J Am Chem Soc.* 2015; 137:685–690. [PubMed: 25551171]
37. He W, Wang L, Sun C, Wu K, He S, Chen J, Wu P, Yu Z. Pt–Sn/ $\gamma\text{-Al}_2\text{O}_3$ -Catalyzed Highly Efficient Direct Synthesis of Secondary and Tertiary Amines and Imines. *Chem Eur J.* 2011; 17:13308–13317. [PubMed: 21997929]
38. Shao Z, Fu S, Wei M, Zhou S, Liu Q. Mild and Selective Cobalt-Catalyzed Chemodivergent Transfer Hydrogenation of Nitriles. *Angew Chem, Int Ed.* 2016; 55:14653–14657.
39. Fang Y-Q, Jacobsen EN. Cooperative, Highly Enantioselective Phosphinothiourea Catalysis of Imine–Allene [3+2] Cycloadditions. *J Am Chem Soc.* 2008; 130:5660–5661. [PubMed: 18393504]
40. Yuan H, Yoo WJ, Miyamura H, Kobayashi S. Discovery of a Metalloenzyme-like Cooperative Catalytic System of Metal Nanoclusters and Catechol Derivatives for the Aerobic Oxidation of Amines. *J Am Chem Soc.* 2012; 134:13970–13973. [PubMed: 22852772]
41. Zhao P-P, Zhou X-F, Dai J-J, Xu H-J. Catalyst-Free Reductive Amination of Aromatic Aldehydes with Ammonium Formate and Hantzsch Ester. *Org Biomol Chem.* 2014; 12:9092–9096. [PubMed: 25295463]
42. Polet D, Alexakis A. Kinetic Study of Various Phosphoramidite Ligands in the Iridium-Catalyzed Allylic Substitution. *Org Lett.* 2005; 7:1621–1624. [PubMed: 15816767]
43. Miriyala B, Bhattacharyya S, Williamson JS. Chemoselective Reductive Alkylation of Ammonia with Carbonyl Compounds: Synthesis of Primary and Symmetrical Secondary Amines. *Tetrahedron.* 2004; 60:1463–1471.
44. Kawahara R, Fujita K, Yamaguchi R. Multialkylation of Aqueous Ammonia with Alcohols Catalyzed by Water-Soluble Cp^*Ir –Ammine Complexes. *J Am Chem Soc.* 2010; 132:15108–15111. [PubMed: 20931960]
45. Kumar P, Cherian SK, Jain R, Show K. Chemoselective Deprotection of N-allylic Amines using DDQ. *Tetrahedron Lett.* 2014; 55:7172–7176.
46. Yamaguchi R, Mingwen Z, Kawagoe S, Asai C, Fujita K. A New Atom-Economical and Selective Synthesis of Secondary and Tertiary Alkylamines by Means of $\text{Cp}^*\text{Iridium}$ Complex Catalyzed Multiple N-Alkylation of Ammonium Salts with Alcohols without Solvent. *Synthesis.* 2009; 7:1220–1223.
47. Petersen LLR-L, Jensen P, Madsen R. Iridium-Catalyzed Condensation of Primary Amines to Form Secondary Amines. *Synthesis.* 2009; 24:4110–4112.

48. Yin Z, Zeng H, Wu J, Zheng S, Zhang G. Cobalt-Catalyzed Synthesis of Aromatic, Aliphatic, and Cyclic Secondary Amines via a “Hydrogen-Borrowing” Strategy. *ACS Catal.* 2016; 6:6546–6550.
49. Fasano V, Radcliffe JE, Ingleson MJ. B(C₆F₅)₃-Catalyzed Reductive Amination using Hydrosilanes. *ACS Catal.* 2016; 6:1793–1798.
50. Ji P, Manna K, Lin Z, Urban A, Greene FX, Lan G, Lin W. Single-Site Cobalt Catalysts at New Zr₈(μ₂-O)₈(μ₂-OH)₄ Metal-Organic Framework Nodes for Highly Active Hydrogenation of Alkenes, Imines, Carbonyls, and Heterocycles. *J Am Chem Soc.* 2016; 138:12234–12242. [PubMed: 27598720]
51. Too PC, Chan GH, Tnay YL, Hirao H, Chiba S. Hydride Reduction by a Sodium Hydride–Iodide Composite. *Angew Chem.* 2016; 128:3783–3787.
52. Corre Y, Iali W, Hamdaoui M, Trivelli X, Djukic J-P, -Niedercorn FA, Michon C. Efficient Hydrosilylation of Imines using Catalysts Based on Iridium(III) Metallocycles. *Catal Sci Tech.* 2015; 5:1452–1458.
53. Champagne PA, Pomarole J, Therien M-E, Benhassine Y, Beaulieu S, Legault CY, Paquin J-F. Enabling Nucleophilic Substitution Reactions of Activated Alkyl Fluorides through Hydrogen Bonding. *Org Lett.* 2013; 15:2210–2213. [PubMed: 23614350]
54. Yagafarov NZ, Usanov DL, Moskovets AP, Kagramanov ND, Maleev VI, Chusov D. Reductive Transformations of Carbonyl Compounds Catalyzed by Rhodium Supported on a Carbon Matrix by using Carbon Monoxide as a Deoxygenative Agent. *Chem Cat Chem.* 2015; 7:2590–2593.
55. Afanasyev OI, Tsygankov AA, Usanov DL, Perekalin DS, Shvydkiy NV, Maleev VI, Kudinov AR, Chusov D. Cyclobutadiene Metal Complexes: A New Class of Highly Selective Catalysts. An Application to Direct Reductive Amination. *ACS Catal.* 2016; 6:2043–2046.
56. Sousa SCA, Fernandes AC. Efficient and Highly Chemoselective Direct Reductive Amination of Aldehydes using the System Silane/Oxorhenium Complexes. *Adv Synth Catal.* 2010; 352:2218–2226.
57. Cushman M, Nagarathnam D, Gopal D, Chakraborti AK, Lin CM, Hamel E. Synthesis and Evaluation of Stilbene and Dihydrostilbene Derivatives as Potential Anticancer Agents that Inhibit Tubulin Polymerization. *J Med Chem.* 1991; 34:2579–2588. [PubMed: 1875350]
58. Bhunia M, Hota PK, Vijaykumar G, Adhikari G, Mandal SK. A Highly Efficient Base-Metal Catalyst: Chemoselective Reduction of Imines to Amines Using An Abnormal-NHC–Fe(0) Complex. *Organometallics.* 2016; 35:2930–2937.
59. Laha JK, Tummalapalli KSS, Jethava KP. Implications of Dynamic Imine Chemistry for the Sustainable Synthesis of Nitrogen Heterocycles via Transimination Followed by Intramolecular Cyclisation. *Org Biomol Chem.* 2016; 14:2473–2479. [PubMed: 26815429]
60. Yang M, Liu F. An Ullmann Coupling of Aryl Iodides and Amines Using an Air-Stable Diazaphospholane Ligand. *J Org Chem.* 2007; 72:8969–8971. [PubMed: 17935348]
61. Akisanya J, Danks TN, Garman RN. Reaction of (1-Azabuta-1, 3-diene)tricarbonyliron(0) Complexes with Sodium Borohydride under Microwave Conditions. *J Organomet Chem.* 2000; 603:240–243.
62. Bollenbach M, Wagner P, Aquino PGV, Bourguignon J-J, Bihel F, Salomé C, Schmitt M. D-Glucose: An Efficient Reducing Agent for a Copper(II)-Mediated Arylation of Primary Amines in Water. *Chem Sus Chem.* 2016; 9:3244–3249.
63. Aziz J, Brion J-D, Hamze A, Alami M. Copper Acetoacetate [Cu(acac)₂]/BINAP-Promoted Csp³-N Bond Formation via Reductive Coupling of N-Tosylhydrazones with Anilines. *Adv Synth Catal.* 2013; 355:2417–2429.

Figure 1.
Reaction Profile for the Coupling of 4-Methoxybenzylamine. 4-Methoxybenzylamine (●),
4c (■) and ArCH=NCH₂Ar (▲).

Figure 2.
Hammett Plot from the Coupling of 4-Methoxyaniline with 4-X-C₆H₄CH₂NH₂ (X = OMe, Me, H, Cl, F, CF₃).

Scheme 1.
Proposed Mechanism of the Deaminative Coupling of Primary Amines

Table 1Catalyst and Ligand Screening Study^a

entry	catalyst	ligand ^b	yield (3a:4a) ^c
1	1	none	27:7
2	1	phenol	52:16
3	1	1,2-catechol	68:20
4	1	aniline	19:6
5	1	2-NH ₂ PhCOMe	28:16
6	1	PhCONH ₂	trace
7	1	1,1'-BINOL	trace
8	1	1,2-C ₆ H ₄ (NH ₂) ₂	27:12
9	1	L1	74:22
10	1	L2	67:6
11	1	L3	62:13
12	1/HBF ₄ ·OEt ₂	L1	65:1
13	2	L1	70:16
14	2/HBF ₄ ·OEt ₂	L1	60:5
15	[Ru(COD)Cl ₂] _x	L1	14:7
16	RuCl ₃ ·3H ₂ O	L1	0
17	(PPh ₃) ₃ (CO)RuH ₂	L1	0
18	[(<i>p</i> -cymene)RuCl ₂] ₂	L1	<1
19	RuHCl(CO)(PCy ₃) ₂	L1	70:15
20	[(PCy ₃) ₂ (CO)(CH ₃ CN) ₂ RuH]BF ₄	L1	0

^aReaction conditions: benzylamine (0.5 mmol), cyclohexylamine (0.7 mmol), catalyst (3 mol %), ligand (10 mol %), chlorobenzene (2 mL), 130 °C, 16 h.

^bSee the Supporting Information for extensive list and structure of ligands.

^cThe product yield was determined by ¹H NMR using C₆Me₆ as the internal standard.

Table 2

Synthesis of Unsymmetric Secondary Amines from the Deaminative Coupling of Primary Amines^a

^aReaction conditions: R-NH₂ (1.0 mmol), R'-NH₂ (1.4 mmol), **1** (0.75 mol %), **L1** (10 mol %), chlorobenzene (2 mL), 130 °C, 16 h. Ar = C₆H₄-4-OMe.

Table 3

Synthesis of Symmetric Secondary Amines^a

<p> 4a X = H (89%) 4b X = Me (94%) 4c X = OMe (86%) 4d X = Cl (92%) 4e X = Ph (85%) 4f X = F (91%) 4g X = CF₃ (84%) </p>	<p> 4h X = OMe (84%) 4i X = Cl (89%) </p>	<p>4j (77%)</p>
<p>4k (61%)</p>	<p>4l d.r. = 7:1 (75%)</p>
<p> 4m R₁ = OMe, R₂ = H (89%) 4n R₁ = H, R₂ = OMe (90%) 4o R₁ = H, R₂ = F (87%) </p>	<p>4p d.r. = 1:1 (93%)</p>	<p>4r (73%)</p>
<p>4s (95%)</p>	<p>4t (89%)</p>	<p> 4u R = <i>n</i>-pentyl (43%)^b 4v R = <i>n</i>-propyl (46%)^b 4w R = 2-furyl (79%) 4x R = CH₂CH₂Ph (42%)^b </p>

^a Reaction conditions: amine (1.0 mmol), **1** (0.75 mol %), **L1** (10 mol %), chlorobenzene (2 mL), 130 °C, 16 h.

^b 40–50% of tertiary amines formed.

Table 4

Synthesis of Unsymmetric Secondary Amines from the Deaminative Coupling of Anilines with Amines^a ^a Reaction conditions: aniline (0.5 mmol), R-NH₂ (0.7 mmol), **1** (0.75 mol %), **L1** (10 mol %), chlorobenzene (2 mL), 140 °C, 20 h.